

# C<sub>60</sub>: Buckminsterfullerene

H. W. KROTO,\* A. W. ALLAF, and S. P. BALM

School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QH, UK

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## I. Introduction

In 1967 Palmer and Shelef wrote the definitive review of the early work on carbon clusters in their article on the composition of carbon vapor.<sup>1</sup> Major advances have however been made in the interim period, and the overall situation has been updated by Weltner and Van Zee<sup>2</sup> who have given a very complete picture of the state of this fascinating field. Although Weltner and Van Zee's review is comprehensive (up to Nov 1, 1988), covering all aspects of carbon cluster properties, recent advances in the story of C<sub>60</sub> buckminsterfullerene (Figure 1) indicate that a specialized review is necessary and timely. The existence of the fullerenes as a family has now been established and it is useful to use a convenient nomenclature such as fullerene-60 or fullerene-70 which can apply to the whole family. There are of course numerous possible C<sub>60</sub> and C<sub>70</sub> cage isomers, however here we shall, in general, mean the most geodesically stable cages for which there is now no doubt in the case of the 60 and 70 atom species—they are (I<sub>h</sub>)fullerene-60 and (D<sub>3h</sub>)fullerene-70 where standard symmetry labels have been added as prefixes. Since the existence of fullerene-60 and its spontaneous creation have ramifications in numerous areas from the properties of carbonaceous solids and microparticles through combustion, thermolysis, and synthetic organic chemistry to the nature of the carbonaceous constituents of space, these implications are also surveyed.

During a series of experiments in 1985 which probed the nature and chemical reactivity of the species produced during the nucleation of a carbon plasma the C<sub>60</sub> species was discovered to be stable by Kroto, Heath, O'Brien, Curl, and Smalley.<sup>3</sup> It was proposed that this



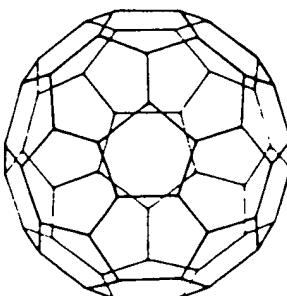
Harry Kroto (left) was educated at Sheffield University and after periods at the National Research Council, Canada (1964–1966), and Bell Telephone Laboratories (1966–1967) went to the University of Sussex where he is now Professor of Chemistry. His research into the production and spectroscopic characterization of new species such as the phosphanaalkynes, phosphaphalkynes, thiocarbonyls, and polyyne led, via radioastronomy studies of interstellar molecules, to carbon cluster beam experiments aimed at understanding stellar chemistry. Wahab Allaf (right) who was educated at Aleppo University (Syria) and Sussex University is carrying out research on carbon clusters and laser chemistry. Simon Balm (center) who is studying cluster beam reactions and astrophysical chemistry was educated at Durham University and Sussex University.

stability was due to geodesic and electronic properties inherent in the truncated icosahedral cage structure shown in Figure 1 and the molecule was named buckminsterfullerene. This novel proposal did not receive instant universal acceptance since it appeared to have been based on highly circumstantial evidence. Indeed it is now clear that there was a significant degree of scepticism in the minds of some with regard to the validity of the proposal, perhaps because the evidence was dispersed among many disparate scientific observations, much like the way that C<sub>60</sub> itself may—we now realize—be involved in many processes involving carbon in the environment and space. However, systems giving rise to C<sub>60</sub> were subjected to many detailed investigations subsequent to the discovery paper,<sup>3</sup> and some important points evolved which are worthy of highlighting:

(i) A wealth of convincing experimental evidence was amassed that showed that C<sub>60</sub> possessed unique physicochemical stability—a conclusion totally independent of the cage structure proposal.

(ii) The fullerene cage proposal was the simplest and most elegant explanation of the unique behavior and no serious alternative explanation was ever presented.

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Figure 1.  $C_{60}$  buckminsterfullerene.<sup>1</sup>

(iii) The proposal was consistent with many earlier observations on bulk carbon and clarified some previously unexplained phenomena in carbon chemistry.

The fullerene structural proposal has recently been confirmed by complementary observations from two groups. Kratschmer, Lamb, Fostiropoulos, and Huffman,<sup>4</sup> in following up their earlier IR investigation (in 1989)<sup>5</sup> which suggested that  $C_{60}$  might be present in arc-processed graphite, extracted a soluble material which formed crystals. The X-ray analysis showed the material to consist of 10-Å diameter spheroidal molecules and supplementary mass spectrometric and infrared data provided the first unequivocal evidence for  $C_{60}$  (and  $C_{70}$ ). In a parallel, independent investigation which probed this same original key observation,<sup>5</sup> Taylor, Hare, Abdul-Sada, and Kroto<sup>6</sup> found that similarly arc-processed graphite gave rise to a 720 mass peak, commensurate with the presence of fullerene-60, and that this material was soluble and could be extracted directly. The extracted  $C_{60}$  compound yielded a single  $^{13}C$  NMR line which proved that all 60 carbon atoms are equivalent as expected for the truncated icosahedral buckminsterfullerene structure. Taylor et al. also showed that  $C_{60}$  and  $C_{70}$  can be separated chromatographically and that the latter has the  $D_{5h}$  prolate, ellipsoidal structure first suggested by Heath et al.<sup>6</sup> These results provide further support for the conjecture that a whole family of fullerenes exists.<sup>7,8</sup>

Since these revelations, which are discussed further in section IX, the fullerene field has exploded and numerous groups are probing various facets of physicochemical properties of the fullerenes. Indeed a new field of carbon chemistry has been born, and the first faltering steps of the promising infant are described in section X. Thus this review is particularly timely as it is written at the precise moment when the final sentence in the last paragraph of the first chapter in the story of the fullerenes has been completed. The opening paragraphs in the next chapter are just being written and they herald a new era in which the flat world of polycyclic aromatic chemistry has been replaced by a postbuckminsterfullerene one in which round structures are favored under certain surprisingly common circumstances.<sup>10</sup> This article reviews the buckminsterfullerene story from the time when it was just a twinkle in the eyes of a few imaginative theoreticians, through the experiments which revealed that it actually formed spontaneously and exhibited stability to the most recent revelations that it could be isolated and did indeed possess the round hollow cage structure as

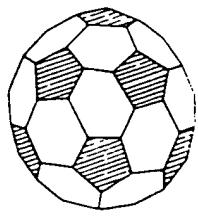


Figure 2. Diagram of  $C_{60}$  next to an icosahedron published in the book *Aromaticity* by Yoshida and Osawa.<sup>14</sup> These authors discuss (in Japanese) the "superaromaticity" which might accompany electron delocalization over a three dimensional truncated icosahedral pure carbon molecule.

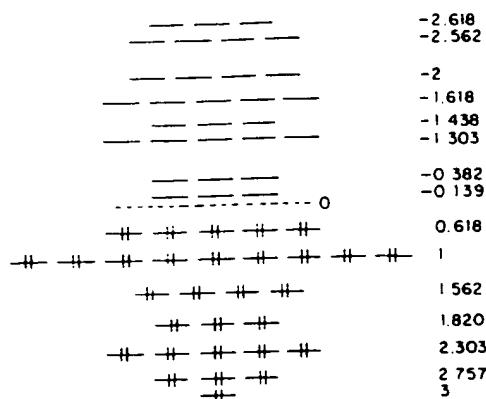
proposed. As many contributions to the story as could be traced by Dec 1990 are included.

### II. Summary of Relevant Carbon Studies Prior to the Discovery of $C_{60}$ Stability

At least part of the reason for the degree of interest engendered by the buckminsterfullerene proposal revolves around its high degree of symmetry. Mankind has always been fascinated by symmetric objects, indeed stone artifacts with the form of the Platonic solids, dating back to neolithic times, have been found in Scotland,<sup>11</sup> indicating that human beings have long had a spiritual affinity with abstract symmetry and an aesthetic fascination for symmetric objects. The truncated icosahedron is one of the Archimedean semi-regular solids; however in hollow form an early example appears in the book *De Divina Proportione* by Fra Lucia Pacioli. A reproduction of this drawing by Leonardo Da Vinci entitled "VCOSEDRON ABSCISVS VACVVS" is to be found in the book *The Unknown Leonardo*,<sup>12</sup> which is rather more accessible than the original!

The  $C_{60}$  molecule itself was first suggested in a most imaginative and prescient paper by Osawa in 1970<sup>13</sup> and discussed further in a chapter on "Superaromaticity" in a book by Yoshida and Osawa<sup>14</sup> in 1971; the original diagram is depicted in Figure 2. An equally imaginative article, which actually predates this work, was written in 1966 by Jones in which he conjectured on the possibility of making large hollow carbon cages.<sup>15,16</sup> The next paper was that of Bochvar and Gal'pern in 1973 who also published a Hückel calculation on  $C_{60}$ .<sup>17,18</sup> In 1980 Davidson published a paper which used graph theory to deduce an algebraic solution of the Hückel calculation for fullerene-60.<sup>19</sup> Davidson's orbital energy level diagram, depicted in Figure 3, was determined by using a calculator, and this paper contains an unusually prescient paragraph in the light of recent observations (particularly those in section VII): "Should such structures or higher homologs ever be rationally synthesized or obtained by pyrolytic routes from carbon polymers, they would be the first manifestations of authentic, discrete three-dimensional aromaticity." Haymet's study<sup>20</sup> on this molecule coincided very closely with its discovery in 1985.<sup>3</sup>

On the experimental front there were many very important early papers on carbon clusters and these have already been reviewed.<sup>12</sup> Perhaps the most interesting early carbon cluster papers (and the ones which in fact actually stimulated the discovery experiments) were

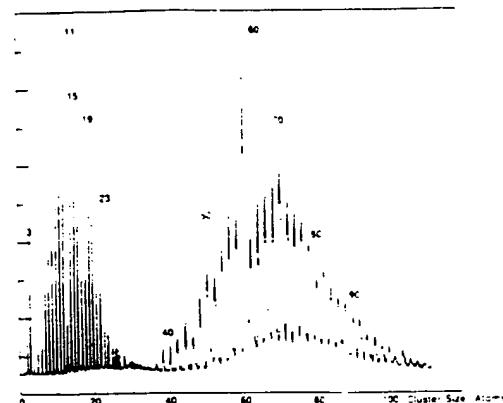


**Figure 3.** The Hückel molecular orbital calculation for buckminsterfullerene was carried out by Bochvar and Gal'pern<sup>17,18</sup> (1973) and Davidson<sup>19</sup> (1980), prior to, and by Haymet<sup>20</sup> (1985) coincidentally with, its discovery. The orbital energy level diagram (units of  $B$ ) depicted here is that published by Davidson<sup>19</sup> who determined it using graph theory to obtain simplified algebraic relations which were evaluated with a calculator (reprinted from ref 19; copyright 1981 Springer-Verlag Publishers).

those published by Hintenberger and co-workers in 1959–63<sup>21–24</sup> in which it was shown that species with up to 33 carbon atoms could form in a carbon arc. The next important advance was made by Rohlfsing, Cox, and Kaldor<sup>25</sup> in 1984 who found that much larger carbon clusters ( $C_n$  with  $n = 30$ –190) could be produced by vaporization of graphite (Figure 4). Rohlfsing et al. used the supersonic nozzle, laser vaporization technique developed by Smalley and co-workers at Rice University<sup>26</sup> in 1981. In this technique clusters are made by laser vaporization of refractory materials into a pulse of helium or argon in the throat of a supersonic nozzle. The vaporized material nucleates in the gas pulse which then expands supersonically into a vacuum chamber where it cools and is skimmed. The skimmed beam passes into a second chamber where the entrained clusters are ionized by a second laser pulse and the cluster ion mass distributions determined by time of flight mass spectrometry (TOF-MS). The mass spectrum observed by Rohlfsing et al.<sup>25</sup> is shown in Figure 4; they pointed out that only ions with *even* numbers of carbon atoms were observable for the new family of clusters with more than 30 carbon atoms. Packing or magic number effects are very weak under these conditions.<sup>27</sup> Bloomfield et al.<sup>28</sup> also studied carbon clusters by the same technique and observed both positive and negative *even* numbered ions. They also studied the fragmentation behavior of the new family and in particular chose the  $C_{60}$  cluster for further study and showed that it could be photodecomposed with 532-nm multiphoton laser radiation.

### III. The Discovery of $C_{60}$ : Buckminsterfullerene

In September 1985 the reactions of carbon clusters were investigated by the Rice/Sussex group.<sup>29,30</sup> These experiments were aimed at simulating the conditions under which carbon nucleates in the atmospheres of cool N-type red giant stars. Circumstantial evidence connected to *sunspots*<sup>31,32</sup> that such stars might be libral-



**Figure 4.** Time-of-flight mass spectrum, observed by Rohlfsing, Cox and Kaldor,<sup>25</sup> of carbon clusters produced by laser vaporization of graphite. In this experiment carbon clusters with 30–190 atoms were detected for the first time. These studies showed that only even-numbered clusters were stable (reprinted from ref 25, copyright 1984 the American Institute of Physics).

sources of the long carbon chain molecules in the interstellar medium and in particular that the formation process might be related in some important way to soot formation.<sup>33</sup> The interstellar cyanopolynes ( $HC_nN$  ( $n = 5$ –11)) were discovered by a synergistic combination of laboratory microwave spectroscopy experiments,<sup>33,34</sup> theoretical analysis,<sup>35</sup> and observational radioastronomy.<sup>36–39</sup> The cluster beam experiments showed convincingly that species such as  $HC_2N$  and  $HC_9N$ , which had been detected in space,<sup>36–38</sup> could be produced by such laboratory simulations of the conditions in carbon stars.<sup>29,30</sup> A second motivation for probing laser vaporization of graphite was the question of whether carbon clusters were associated with the so-called diffuse interstellar bands as Douglas had proposed in 1977.<sup>40</sup> The development of resonant 2-photon ionization in conjunction with the cluster beam technique to obtain the high-resolution spectrum of  $SiC_2$  by Michalopoulos et al.<sup>41</sup> suggested that the electronic spectra of carbon clusters might be accessible by this technique. During the course of the experiments<sup>29,30</sup> which probed the behavior of the pure carbon clusters a striking discovery was made—under some clustering conditions the 720 mass peak appeared to be extremely strong (Figure 5).<sup>3</sup> Indeed the intensity of the  $C_{60}$  peak, relative to the adjacent cluster distribution, could be varied dramatically just by altering the conditions. In particular, conditions could be found for which the mass spectrum was totally dominated by the  $C_{60}$  peak—at least in the mass range accessible (Figure 6). It was concluded that  $C_{60}$  must be particularly stable to further nucleation and it was proposed that this might be explained by the geodesic factors inherent in a truncated icosahedral cage structure in which all the atoms were connected by  $sp^2$  bonds and the remaining 60  $\pi$  electrons distributed in such a way that aromatic character appeared highly likely.<sup>3</sup>

In these experiments it was found that the  $C_{70}$  peak also showed clear enhancement although to a lesser extent; the  $C_{60}/C_{70}$  ratio was ca. 5/1 in general. In previous experiments<sup>25,27,28</sup> the  $C_{60}/(C_{58} \text{ or } C_{62})$  ratio was ca. 2/1 (Figure 4) whereas in the new experiments

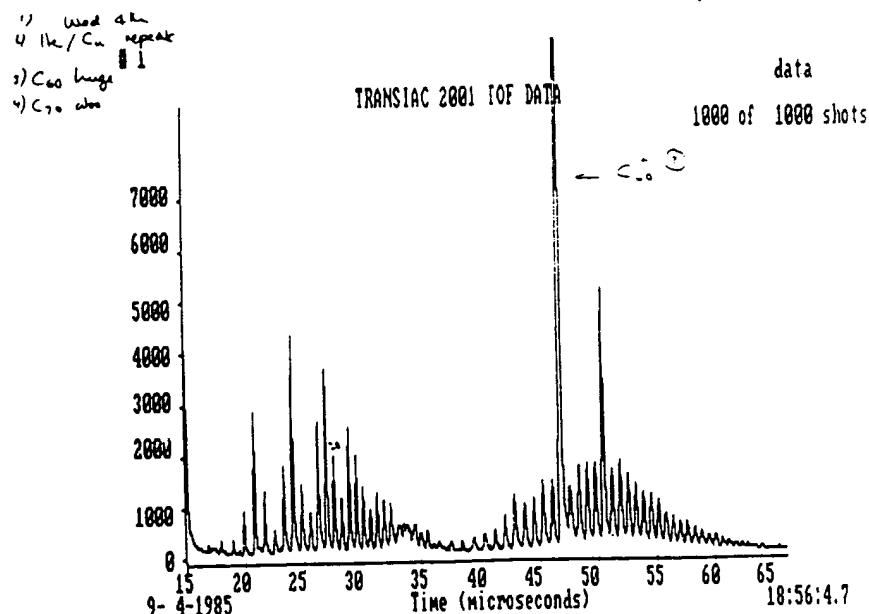


Figure 5. Time-of-flight mass spectrum of carbon clusters produced by laser vaporization of graphite (Sept 4, 1985) under conditions which first exhibited the dominance of the  $C_{60}$  cluster and led to the recognition that 60 might be a "magic" number.

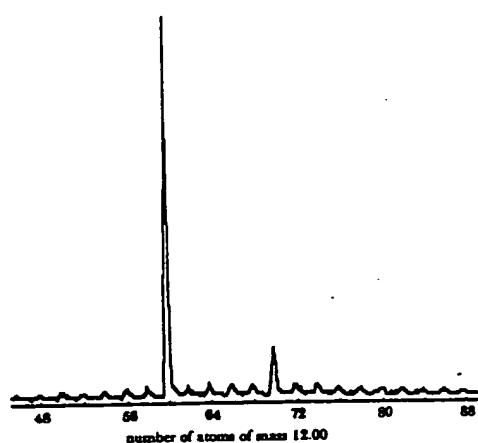


Figure 6. Time-of-flight mass spectrum of carbon clusters produced by laser vaporization of graphite under the optimum conditions for observation of a dominant  $C_{60}$  cluster signal.<sup>3</sup> Note also the prominence of  $C_{70}$ .

conditions were found in which a ratio of 20/1 or more was achieved (Figure 6). It was soon realized that although  $C_{60}$  generally appeared fairly special, the conditions under which it appeared dominant were rather unusual. They were conditions in which the major fraction of the carbon had nucleated to form macroscopic particles too large to be detectable by the mass spectrometer. Thus it was recognized that the signal shown in Figure 6 shows the "small" carbon species which remain when the microparticles have formed. Due to the fact that geodesic structural concepts were a guide to the hollow cage structural explanation that

Henriacosahepta-29,29,0,0<sup>1,1</sup>,0<sup>2,2</sup>,0<sup>3,3</sup>,0<sup>4,4</sup>,0<sup>5,5</sup>,0<sup>6,6</sup>,0<sup>7,7</sup>,0<sup>8,8</sup>,0<sup>9,9</sup>,0<sup>10,10</sup>,0<sup>11,11</sup>,0<sup>12,12</sup>,0<sup>13,13</sup>,0<sup>14,14</sup>,0<sup>15,15</sup>,0<sup>16,16</sup>,0<sup>17,17</sup>,0<sup>18,18</sup>,0<sup>19,19</sup>,0<sup>20,20</sup>,0<sup>21,21</sup>,0<sup>22,22</sup>,0<sup>23,23</sup>,0<sup>24,24</sup>,0<sup>25,25</sup>,0<sup>26,26</sup>,0<sup>27,27</sup>,0<sup>28,28</sup>,0<sup>29,29</sup>,0<sup>30,30</sup>,0<sup>31,31</sup>,0<sup>32,32</sup>,0<sup>33,33</sup>,0<sup>34,34</sup>,0<sup>35,35</sup>,0<sup>36,36</sup>,0<sup>37,37</sup>,0<sup>38,38</sup>,0<sup>39,39</sup>,0<sup>40,40</sup>,0<sup>41,41</sup>,0<sup>42,42</sup>,0<sup>43,43</sup>,0<sup>44,44</sup>,0<sup>45,45</sup>,0<sup>46,46</sup>,0<sup>47,47</sup>,0<sup>48,48</sup>,0<sup>49,49</sup>,0<sup>50,50</sup>,0<sup>51,51</sup>,0<sup>52,52</sup>,0<sup>53,53</sup>,0<sup>54,54</sup>,0<sup>55,55</sup>,0<sup>56,56</sup>,0<sup>57,57</sup>,0<sup>58,58</sup>,0<sup>59,59</sup>,0<sup>60,60</sup>,0<sup>61,61</sup>,0<sup>62,62</sup>,0<sup>63,63</sup>,0<sup>64,64</sup>,0<sup>65,65</sup>,0<sup>66,66</sup>,0<sup>67,67</sup>,0<sup>68,68</sup>,0<sup>69,69</sup>,0<sup>70,70</sup>,0<sup>71,71</sup>,0<sup>72,72</sup>,0<sup>73,73</sup>,0<sup>74,74</sup>,0<sup>75,75</sup>,0<sup>76,76</sup>,0<sup>77,77</sup>,0<sup>78,78</sup>,0<sup>79,79</sup>,0<sup>80,80</sup>,0<sup>81,81</sup>,0<sup>82,82</sup>,0<sup>83,83</sup>,0<sup>84,84</sup>,0<sup>85,85</sup>,0<sup>86,86</sup>,0<sup>87,87</sup>,0<sup>88,88</sup>,0<sup>89,89</sup>,0<sup>90,90</sup>,0<sup>91,91</sup>,0<sup>92,92</sup>,0<sup>93,93</sup>,0<sup>94,94</sup>,0<sup>95,95</sup>,0<sup>96,96</sup>,0<sup>97,97</sup>,0<sup>98,98</sup>,0<sup>99,99</sup>,0<sup>100,100</sup>,0<sup>101,101</sup>,0<sup>102,102</sup>,0<sup>103,103</sup>,0<sup>104,104</sup>,0<sup>105,105</sup>,0<sup>106,106</sup>,0<sup>107,107</sup>,0<sup>108,108</sup>,0<sup>109,109</sup>,0<sup>110,110</sup>,0<sup>111,111</sup>,0<sup>112,112</sup>,0<sup>113,113</sup>,0<sup>114,114</sup>,0<sup>115,115</sup>,0<sup>116,116</sup>,0<sup>117,117</sup>,0<sup>118,118</sup>,0<sup>119,119</sup>,0<sup>120,120</sup>,0<sup>121,121</sup>,0<sup>122,122</sup>,0<sup>123,123</sup>,0<sup>124,124</sup>,0<sup>125,125</sup>,0<sup>126,126</sup>,0<sup>127,127</sup>,0<sup>128,128</sup>,0<sup>129,129</sup>,0<sup>130,130</sup>,0<sup>131,131</sup>,0<sup>132,132</sup>,0<sup>133,133</sup>,0<sup>134,134</sup>,0<sup>135,135</sup>,0<sup>136,136</sup>,0<sup>137,137</sup>,0<sup>138,138</sup>,0<sup>139,139</sup>,0<sup>140,140</sup>,0<sup>141,141</sup>,0<sup>142,142</sup>,0<sup>143,143</sup>,0<sup>144,144</sup>,0<sup>145,145</sup>,0<sup>146,146</sup>,0<sup>147,147</sup>,0<sup>148,148</sup>,0<sup>149,149</sup>,0<sup>150,150</sup>,0<sup>151,151</sup>,0<sup>152,152</sup>,0<sup>153,153</sup>,0<sup>154,154</sup>,0<sup>155,155</sup>,0<sup>156,156</sup>,0<sup>157,157</sup>,0<sup>158,158</sup>,0<sup>159,159</sup>,0<sup>160,160</sup>,0<sup>161,161</sup>,0<sup>162,162</sup>,0<sup>163,163</sup>,0<sup>164,164</sup>,0<sup>165,165</sup>,0<sup>166,166</sup>,0<sup>167,167</sup>,0<sup>168,168</sup>,0<sup>169,169</sup>,0<sup>170,170</sup>,0<sup>171,171</sup>,0<sup>172,172</sup>,0<sup>173,173</sup>,0<sup>174,174</sup>,0<sup>175,175</sup>,0<sup>176,176</sup>,0<sup>177,177</sup>,0<sup>178,178</sup>,0<sup>179,179</sup>,0<sup>180,180</sup>,0<sup>181,181</sup>,0<sup>182,182</sup>,0<sup>183,183</sup>,0<sup>184,184</sup>,0<sup>185,185</sup>,0<sup>186,186</sup>,0<sup>187,187</sup>,0<sup>188,188</sup>,0<sup>189,189</sup>,0<sup>190,190</sup>,0<sup>191,191</sup>,0<sup>192,192</sup>,0<sup>193,193</sup>,0<sup>194,194</sup>,0<sup>195,195</sup>,0<sup>196,196</sup>,0<sup>197,197</sup>,0<sup>198,198</sup>,0<sup>199,199</sup>,0<sup>200,200</sup>,0<sup>201,201</sup>,0<sup>202,202</sup>,0<sup>203,203</sup>,0<sup>204,204</sup>,0<sup>205,205</sup>,0<sup>206,206</sup>,0<sup>207,207</sup>,0<sup>208,208</sup>,0<sup>209,209</sup>,0<sup>210,210</sup>,0<sup>211,211</sup>,0<sup>212,212</sup>,0<sup>213,213</sup>,0<sup>214,214</sup>,0<sup>215,215</sup>,0<sup>216,216</sup>,0<sup>217,217</sup>,0<sup>218,218</sup>,0<sup>219,219</sup>,0<sup>220,220</sup>,0<sup>221,221</sup>,0<sup>222,222</sup>,0<sup>223,223</sup>,0<sup>224,224</sup>,0<sup>225,225</sup>,0<sup>226,226</sup>,0<sup>227,227</sup>,0<sup>228,228</sup>,0<sup>229,229</sup>,0<sup>230,230</sup>,0<sup>231,231</sup>,0<sup>232,232</sup>,0<sup>233,233</sup>,0<sup>234,234</sup>,0<sup>235,235</sup>,0<sup>236,236</sup>,0<sup>237,237</sup>,0<sup>238,238</sup>,0<sup>239,239</sup>,0<sup>240,240</sup>,0<sup>241,241</sup>,0<sup>242,242</sup>,0<sup>243,243</sup>,0<sup>244,244</sup>,0<sup>245,245</sup>,0<sup>246,246</sup>,0<sup>247,247</sup>,0<sup>248,248</sup>,0<sup>249,249</sup>,0<sup>250,250</sup>,0<sup>251,251</sup>,0<sup>252,252</sup>,0<sup>253,253</sup>,0<sup>254,254</sup>,0<sup>255,255</sup>,0<sup>256,256</sup>,0<sup>257,257</sup>,0<sup>258,258</sup>,0<sup>259,259</sup>,0<sup>260,260</sup>,0<sup>261,261</sup>,0<sup>262,262</sup>,0<sup>263,263</sup>,0<sup>264,264</sup>,0<sup>265,265</sup>,0<sup>266,266</sup>,0<sup>267,267</sup>,0<sup>268,268</sup>,0<sup>269,269</sup>,0<sup>270,270</sup>,0<sup>271,271</sup>,0<sup>272,272</sup>,0<sup>273,273</sup>,0<sup>274,274</sup>,0<sup>275,275</sup>,0<sup>276,276</sup>,0<sup>277,277</sup>,0<sup>278,278</sup>,0<sup>279,279</sup>,0<sup>280,280</sup>,0<sup>281,281</sup>,0<sup>282,282</sup>,0<sup>283,283</sup>,0<sup>284,284</sup>,0<sup>285,285</sup>,0<sup>286,286</sup>,0<sup>287,287</sup>,0<sup>288,288</sup>,0<sup>289,289</sup>,0<sup>290,290</sup>,0<sup>291,291</sup>,0<sup>292,292</sup>,0<sup>293,293</sup>,0<sup>294,294</sup>,0<sup>295,295</sup>,0<sup>296,296</sup>,0<sup>297,297</sup>,0<sup>298,298</sup>,0<sup>299,299</sup>,0<sup>300,300</sup>,0<sup>301,301</sup>,0<sup>302,302</sup>,0<sup>303,303</sup>,0<sup>304,304</sup>,0<sup>305,305</sup>,0<sup>306,306</sup>,0<sup>307,307</sup>,0<sup>308,308</sup>,0<sup>309,309</sup>,0<sup>310,310</sup>,0<sup>311,311</sup>,0<sup>312,312</sup>,0<sup>313,313</sup>,0<sup>314,314</sup>,0<sup>315,315</sup>,0<sup>316,316</sup>,0<sup>317,317</sup>,0<sup>318,318</sup>,0<sup>319,319</sup>,0<sup>320,320</sup>,0<sup>321,321</sup>,0<sup>322,322</sup>,0<sup>323,323</sup>,0<sup>324,324</sup>,0<sup>325,325</sup>,0<sup>326,326</sup>,0<sup>327,327</sup>,0<sup>328,328</sup>,0<sup>329,329</sup>,0<sup>330,330</sup>,0<sup>331,331</sup>,0<sup>332,332</sup>,0<sup>333,333</sup>,0<sup>334,334</sup>,0<sup>335,335</sup>,0<sup>336,336</sup>,0<sup>337,337</sup>,0<sup>338,338</sup>,0<sup>339,339</sup>,0<sup>340,340</sup>,0<sup>341,341</sup>,0<sup>342,342</sup>,0<sup>343,343</sup>,0<sup>344,344</sup>,0<sup>345,345</sup>,0<sup>346,346</sup>,0<sup>347,347</sup>,0<sup>348,348</sup>,0<sup>349,349</sup>,0<sup>350,350</sup>,0<sup>351,351</sup>,0<sup>352,352</sup>,0<sup>353,353</sup>,0<sup>354,354</sup>,0<sup>355,355</sup>,0<sup>356,356</sup>,0<sup>357,357</sup>,0<sup>358,358</sup>,0<sup>359,359</sup>,0<sup>360,360</sup>,0<sup>361,361</sup>,0<sup>362,362</sup>,0<sup>363,363</sup>,0<sup>364,364</sup>,0<sup>365,365</sup>,0<sup>366,366</sup>,0<sup>367,367</sup>,0<sup>368,368</sup>,0<sup>369,369</sup>,0<sup>370,370</sup>,0<sup>371,371</sup>,0<sup>372,372</sup>,0<sup>373,373</sup>,0<sup>374,374</sup>,0<sup>375,375</sup>,0<sup>376,376</sup>,0<sup>377,377</sup>,0<sup>378,378</sup>,0<sup>379,379</sup>,0<sup>380,380</sup>,0<sup>381,381</sup>,0<sup>382,382</sup>,0<sup>383,383</sup>,0<sup>384,384</sup>,0<sup>385,385</sup>,0<sup>386,386</sup>,0<sup>387,387</sup>,0<sup>388,388</sup>,0<sup>389,389</sup>,0<sup>390,390</sup>,0<sup>391,391</sup>,0<sup>392,392</sup>,0<sup>393,393</sup>,0<sup>394,394</sup>,0<sup>395,395</sup>,0<sup>396,396</sup>,0<sup>397,397</sup>,0<sup>398,398</sup>,0<sup>399,399</sup>,0<sup>400,400</sup>,0<sup>401,401</sup>,0<sup>402,402</sup>,0<sup>403,403</sup>,0<sup>404,404</sup>,0<sup>405,405</sup>,0<sup>406,406</sup>,0<sup>407,407</sup>,0<sup>408,408</sup>,0<sup>409,409</sup>,0<sup>410,410</sup>,0<sup>411,411</sup>,0<sup>412,412</sup>,0<sup>413,413</sup>,0<sup>414,414</sup>,0<sup>415,415</sup>,0<sup>416,416</sup>,0<sup>417,417</sup>,0<sup>418,418</sup>,0<sup>419,419</sup>,0<sup>420,420</sup>,0<sup>421,421</sup>,0<sup>422,422</sup>,0<sup>423,423</sup>,0<sup>424,424</sup>,0<sup>425,425</sup>,0<sup>426,426</sup>,0<sup>427,427</sup>,0<sup>428,428</sup>,0<sup>429,429</sup>,0<sup>430,430</sup>,0<sup>431,431</sup>,0<sup>432,432</sup>,0<sup>433,433</sup>,0<sup>434,434</sup>,0<sup>435,435</sup>,0<sup>436,436</sup>,0<sup>437,437</sup>,0<sup>438,438</sup>,0<sup>439,439</sup>,0<sup>440,440</sup>,0<sup>441,441</sup>,0<sup>442,442</sup>,0<sup>443,443</sup>,0<sup>444,444</sup>,0<sup>445,445</sup>,0<sup>446,446</sup>,0<sup>447,447</sup>,0<sup>448,448</sup>,0<sup>449,449</sup>,0<sup>450,450</sup>,0<sup>451,451</sup>,0<sup>452,452</sup>,0<sup>453,453</sup>,0<sup>454,454</sup>,0<sup>455,455</sup>,0<sup>456,456</sup>,0<sup>457,457</sup>,0<sup>458,458</sup>,0<sup>459,459</sup>,0<sup>460,460</sup>,0<sup>461,461</sup>,0<sup>462,462</sup>,0<sup>463,463</sup>,0<sup>464,464</sup>,0<sup>465,465</sup>,0<sup>466,466</sup>,0<sup>467,467</sup>,0<sup>468,468</sup>,0<sup>469,469</sup>,0<sup>470,470</sup>,0<sup>471,471</sup>,0<sup>472,472</sup>,0<sup>473,473</sup>,0<sup>474,474</sup>,0<sup>475,475</sup>,0<sup>476,476</sup>,0<sup>477,477</sup>,0<sup>478,478</sup>,0<sup>479,479</sup>,0<sup>480,480</sup>,0<sup>481,481</sup>,0<sup>482,482</sup>,0<sup>483,483</sup>,0<sup>484,484</sup>,0<sup>485,485</sup>,0<sup>486,486</sup>,0<sup>487,487</sup>,0<sup>488,488</sup>,0<sup>489,489</sup>,0<sup>490,490</sup>,0<sup>491,491</sup>,0<sup>492,492</sup>,0<sup>493,493</sup>,0<sup>494,494</sup>,0<sup>495,495</sup>,0<sup>496,496</sup>,0<sup>497,497</sup>,0<sup>498,498</sup>,0<sup>499,499</sup>,0<sup>500,500</sup>,0<sup>501,501</sup>,0<sup>502,502</sup>,0<sup>503,503</sup>,0<sup>504,504</sup>,0<sup>505,505</sup>,0<sup>506,506</sup>,0<sup>507,507</sup>,0<sup>508,508</sup>,0<sup>509,509</sup>,0<sup>510,510</sup>,0<sup>511,511</sup>,0<sup>512,512</sup>,0<sup>513,513</sup>,0<sup>514,514</sup>,0<sup>515,515</sup>,0<sup>516,516</sup>,0<sup>517,517</sup>,0<sup>518,518</sup>,0<sup>519,519</sup>,0<sup>520,520</sup>,0<sup>521,521</sup>,0<sup>522,522</sup>,0<sup>523,523</sup>,0<sup>524,524</sup>,0<sup>525,525</sup>,0<sup>526,526</sup>,0<sup>527,527</sup>,0<sup>528,528</sup>,0<sup>529,529</sup>,0<sup>530,530</sup>,0<sup>531,531</sup>,0<sup>532,532</sup>,0<sup>533,533</sup>,0<sup>534,534</sup>,0<sup>535,535</sup>,0<sup>536,536</sup>,0<sup>537,537</sup>,0<sup>538,538</sup>,0<sup>539,539</sup>,0<sup>540,540</sup>,0<sup>541,541</sup>,0<sup>542,542</sup>,0<sup>543,543</sup>,0<sup>544,544</sup>,0<sup>545,545</sup>,0<sup>546,546</sup>,0<sup>547,547</sup>,0<sup>548,548</sup>,0<sup>549,549</sup>,0<sup>550,550</sup>,0<sup>551,551</sup>,0<sup>552,552</sup>,0<sup>553,553</sup>,0<sup>554,554</sup>,0<sup>555,555</sup>,0<sup>556,556</sup>,0<sup>557,557</sup>,0<sup>558,558</sup>,0<sup>559,559</sup>,0<sup>560,560</sup>,0<sup>561,561</sup>,0<sup>562,562</sup>,0<sup>563,563</sup>,0<sup>564,564</sup>,0<sup>565,565</sup>,0<sup>566,566</sup>,0<sup>567,567</sup>,0<sup>568,568</sup>,0<sup>569,569</sup>,0<sup>570,570</sup>,0<sup>571,571</sup>,0<sup>572,572</sup>,0<sup>573,573</sup>,0<sup>574,574</sup>,0<sup>575,575</sup>,0<sup>576,576</sup>,0<sup>577,577</sup>,0<sup>578,578</sup>,0<sup>579,579</sup>,0<sup>580,580</sup>,0<sup>581,581</sup>,0<sup>582,582</sup>,0<sup>583,583</sup>,0<sup>584,584</sup>,0<sup>585,585</sup>,0<sup>586,586</sup>,0<sup>587,587</sup>,0<sup>588,588</sup>,0<sup>589,589</sup>,0<sup>590,590</sup>,0<sup>591,591</sup>,0<sup>592,592</sup>,0<sup>593,593</sup>,0<sup>594,594</sup>,0<sup>595,595</sup>,0<sup>596,596</sup>,0<sup>597,597</sup>,0<sup>598,598</sup>,0<sup>599,599</sup>,0<sup>600,600</sup>,0<sup>601,601</sup>,0<sup>602,602</sup>,0<sup>603,603</sup>,0<sup>604,604</sup>,0<sup>605,605</sup>,0<sup>606,606</sup>,0<sup>607,607</sup>,0<sup>608,608</sup>,0<sup>609,609</sup>,0<sup>610,610</sup>,0<sup>611,611</sup>,0<sup>612,612</sup>,0<sup>613,613</sup>,0<sup>614,614</sup>,0<sup>615,615</sup>,0<sup>616,616</sup>,0<sup>617,617</sup>,0<sup>618,618</sup>,0<sup>619,619</sup>,0<sup>620,620</sup>,0<sup>621,621</sup>,0<sup>622,622</sup>,0<sup>623,623</sup>,0<sup>624,624</sup>,0<sup>625,625</sup>,0<sup>626,626</sup>,0<sup>627,627</sup>,0<sup>628,628</sup>,0<sup>629,629</sup>,0<sup>630,630</sup>,0<sup>631,631</sup>,0<sup>632,632</sup>,0<sup>633,633</sup>,0<sup>634,634</sup>,0<sup>635,635</sup>,0<sup>636,636</sup>,0<sup>637,637</sup>,0<sup>638,638</sup>,0<sup>639,639</sup>,0<sup>640,640</sup>,0<sup>641,641</sup>,0<sup>642,642</sup>,0<sup>643,643</sup>,0<sup>644,644</sup>,0<sup>645,645</sup>,0<sup>646,646</sup>,0<sup>647,647</sup>,0<sup>648,648</sup>,0<sup>649,649</sup>,0<sup>650,650</sup>,0<sup>651,651</sup>,0<sup>652,652</sup>,0<sup>653,653</sup>,0<sup>654,654</sup>,0<sup>655,655</sup>,0<sup>656,656</sup>,0<sup>657,657</sup>,0<sup>658,658</sup>,0<sup>659,659</sup>,0<sup>660,660</sup>,0<sup>661,661</sup>,0<sup>662,662</sup>,0<sup>663,663</sup>,0<sup>664,664</sup>,0<sup>665,665</sup>,0<sup>666,666</sup>,0<sup>667,667</sup>,0<sup>668,668</sup>,0<sup>669,669</sup>,0<sup>670,670</sup>,0<sup>671,671</sup>,0<sup>672,672</sup>,0<sup>673,673</sup>,0<sup>674,674</sup>,0<sup>675,675</sup>,0<sup>676,676</sup>,0<sup>677,677</sup>,0<sup>678,678</sup>,0<sup>679,679</sup>,0<sup>680,680</sup>,0<sup>681,681</sup>,0<sup>682,682</sup>,0<sup>683,683</sup>,0<sup>684,684</sup>,0<sup>685,685</sup>,0<sup>686,686</sup>,0<sup>687,687</sup>,0<sup>688,688</sup>,0<sup>689,689</sup>,0<sup>690,690</sup>,0<sup>691,691</sup>,0<sup>692,692</sup>,0<sup>693,693</sup>,0<sup>694,694</sup>,0<sup>695,695</sup>,0<sup>696,696</sup>,0<sup>697,697</sup>,0<sup>698,698</sup>,0<sup>699,699</sup>,0<sup>700,700</sup>,0<sup>701,701</sup>,0<sup>702,702</sup>,0<sup>703,703</sup>,0<sup>704,704</sup>,0<sup>705,705</sup>,0<sup>706,706</sup>,0<sup>707,707</sup>,0<sup>708,708</sup>,0<sup>709,709</sup>,0<sup>710,710</sup>,0<sup>711,711</sup>,0<sup>712,712</sup>,0<sup>713,713</sup>,0<sup>714,714</sup>,0<sup>715,715</sup>,0<sup>716,716</sup>,0<sup>717,717</sup>,0<sup>718,718</sup>,0<sup>719,719</sup>,0<sup>720,720</sup>,0<sup>721,721</sup>,0<sup>722,722</sup>,0<sup>723,723</sup>,0<sup>724,724</sup>,0<sup>725,725</sup>,0<sup>726,726</sup>,0<sup>727,727</sup>,0<sup>728,728</sup>,0<sup>729,729</sup>,0<sup>730,730</sup>,0<sup>731,731</sup>,0<sup>732,732</sup>,0<sup>733,733</sup>,0<sup>734,734</sup>,0<sup>735,735</sup>,0<sup>736,736</sup>,0<sup>737,737</sup>,0<sup>738,738</sup>,0<sup>739,739</sup>,0<sup>740,740</sup>,0<sup>741,741</sup>,0<sup>742,742</sup>,0<sup>743,743</sup>,0<sup>744,744</sup>,0<sup>745,745</sup>,0<sup>746,746</sup>,0<sup>747,747</sup>,0<sup>748,748</sup>,0<sup>749,749</sup>,0<sup>750,750</sup>,0<sup>751,751</sup>,0<sup>752,752</sup>,0<sup>753,753</sup>,0<sup>754,754</sup>,0<sup>755,755</sup>,0<sup>756,756</sup>,0<sup>757,757</sup>,0<sup>758,758</sup>,0<sup>759,759</sup>,0<sup>760,760</sup>,0<sup>761,761</sup>,0<sup>762,762</sup>,0<sup>763,763</sup>,0<sup>764,764</sup>,0<sup>765,765</sup>,0<sup>766,766</sup>,0<sup>767,767</sup>,0<sup>768,768</sup>,0<sup>769,769</sup>,0<sup>770,770</sup>,0<sup>771,771</sup</sup>

work has been carried out. Two complementary accounts covering many of the important general implications and experimental observations have been given by Kroto<sup>50</sup> and Curl and Smalley<sup>51</sup>. More focused accounts have also been published dealing mainly with experimental observations,<sup>52-54</sup> astrophysical implications,<sup>42,55-58</sup> symmetry and structure considerations of fullerene-60, and the icosahedral giant fullerenes.<sup>59-61</sup> The chemical implications have also been discussed by Kroto<sup>61</sup> and Kroto and Walton.<sup>10</sup> Hirota<sup>62</sup> and Heath<sup>63</sup> discuss fullerene-60 as well as other novel carbon molecules.

#### IV. Sources of C<sub>60</sub>

In the original work, which showed how conditions could be achieved to produce a signal in which the C<sub>60</sub> peak was dominant, the pulsed nozzle/laser vaporization technique<sup>26</sup> was used to produce the clusters from a graphite target and photoionization TOF-MS used to detect them. The laser-produced plasma expanded into a high pressure (ca. 1-10 atm) of He and the target graphite surface was continually replenished so that the surface remained essentially flat. A nozzle extender was used to increase the clustering time prior to expansion to ca. 100  $\mu$ s and the high He pressure increased the nucleation rate. Although initially it was conjectured that perhaps graphitic sheet fragments might have been ablated from the graphite target and rearranged into the buckminsterfullerene structure, subsequent considerations suggested that C<sub>60</sub> was more likely to have formed by nucleation from carbon vapor consisting, at least initially, of C atoms and very small carbon molecules.<sup>52</sup> Negative ion distributions produced by crossing a laser with the cluster beam just as it exited the nozzle<sup>64</sup> have been studied, and the relationship between these and positive and negative ion distributions, obtained directly from the vaporization zone (i.e. without photoionization), has been discussed by Hahn et al.<sup>65</sup> and O'Brien et al.<sup>66</sup> The consensus of opinion was that C<sub>60</sub> appeared to exhibit special behavior whether charged (positive or negative) or neutral and that the nucleation rate order was neutrals > cations > anions.<sup>66</sup> Very detailed discussion of the conditions under which C<sub>60</sub> appears to be special has been given by Cox et al.<sup>67</sup> These studies are discussed in more detail in section V.

Carbon cluster distributions exhibiting dominant C<sub>60</sub><sup>+</sup> signals, can be produced in another way as O'Keefe, Ross, and Baronavski<sup>68</sup> and Pradel et al.<sup>69</sup> have shown using high vacuum TOF-MS. In these experiments the graphite target is inside the mass spectrometer vacuum system and remains stationary. After several laser pulses a hole is drilled in the graphite and nucleation appears to occur in the cavity. McElvany et al.,<sup>70</sup> using ICR-MS techniques, have shown that if the axis of the laser-drilled hole is aligned parallel to the trapping magnetic field a strong C<sub>60</sub><sup>+</sup> signal predominates in the mass spectrum. In a study of the small cluster distribution, McElvany, Dunlap, and O'Keefe<sup>71</sup> found that the vaporization of a diamond target produces the same distribution as does graphite. This result indicates that the clusters appear to be produced by nucleation of atomic/molecular carbon vapor rather than by a process involving the ablation of bulk fragments from the target. Moller and Rothman<sup>72</sup> have modified the original laser

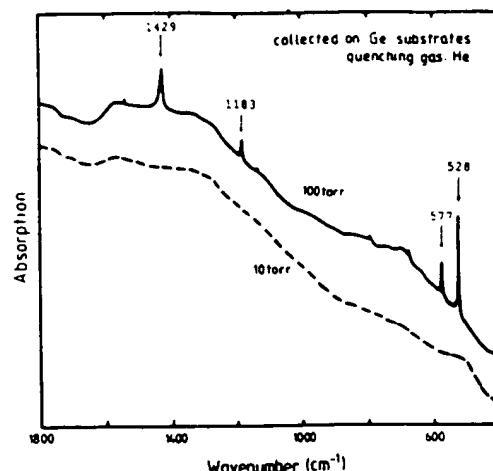
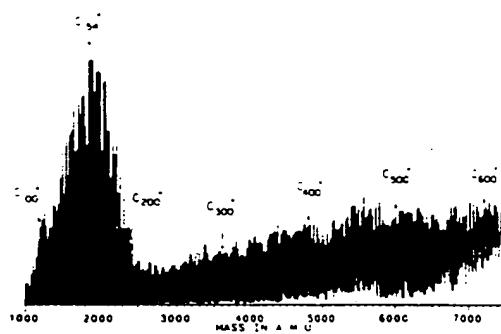


Figure 8. Infrared absorption spectrum observed in 1989 by Krätschmer, Fostiropoulos, and Huffman<sup>57,64</sup> from carbon produced by arc-discharge processing. Krätschmer et al. made the perceptive observation that the four sharp absorption features indicated might belong to fullerene-60. The frequencies were tantalizingly consistent with theoretical predictions (section VIII) for the fundamental vibrations of fullerene-60 (reprinted from ref 74; copyright 1990 Elsevier Science Publishers).

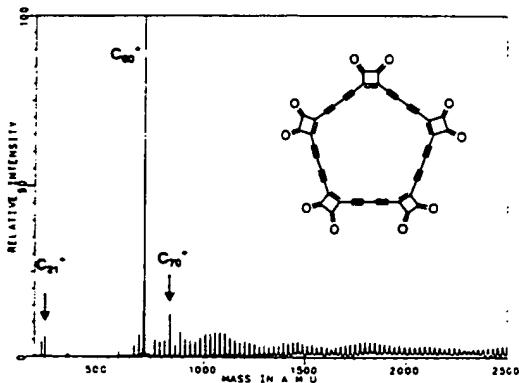
vaporization procedure for producing C<sub>60</sub><sup>3</sup> in order to deposit material on a film. They have shown that the mass spectrum obtained by subsequent laser desorption of the resulting material yields a very similar cluster distribution to that of the cluster beam experiments. They have also carried out isotope scrambling measurements<sup>73</sup> supporting the conclusion that C<sub>60</sub> is assembled from small carbon species in the gas phase after vaporization (see section VI).

A fascinating and ultimately key observation was described in September 1989 by the Heidelberg/Tucson group: Krätschmer, Fostiropoulos, and Huffman<sup>57,64</sup> who detected four weak bands in the infrared spectrum of a film deposited from a carbon arc under argon (Figure 8). Krätschmer et al. pointed out that the vibrational frequencies of the four bands (and associated <sup>13</sup>C shifts) observed were in tantalizingly close agreement with theoretical estimates for fullerene-60 (details in sections VIII and IX).

Several other interesting studies have shown that laser vaporization of a wide variety of carbonaceous target materials (other than pure carbon) also yields a dominant C<sub>60</sub> signal: e.g. carbon films (Creasy and Brenna<sup>75</sup>), polymers such as polyimides (Creasy and Brenna,<sup>76</sup> and Campbell et al.<sup>77-79</sup>), coal (Greenwood et al.<sup>80</sup>), polycyclic aromatic hydrocarbons (Giardini-Guidoni et al.,<sup>81</sup> and Lineman et al.<sup>82,83</sup>). Last but not least, So and Wilkins<sup>84</sup> have shown that C<sub>60</sub> can be detected by laser desorption of soot! In fact they have observed even-numbered carbon clusters with as many as 600 carbon atoms (Figure 9). This result and similar experiments may indicate that giant fullerenes may also be forming.<sup>85</sup> All experiments show that conditions can be found in which the C<sub>60</sub><sup>+</sup> peak is either prominent or dominant. However conditions also exist for which this is not the case.<sup>86</sup> It is likely that the availability of many other pathways to "organic" (H-containing species) may be responsible for some of the latter observations.



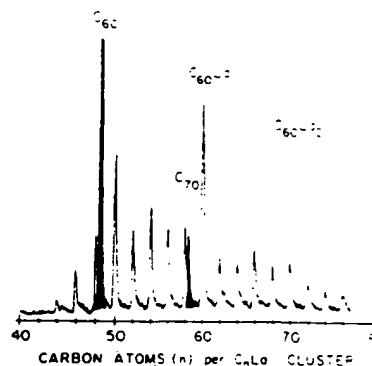
**Figure 9.** Laser desorption Fourier transform mass spectrum, observed by So and Wilkins,<sup>44</sup> of soot deposited on a KCl-coated stainless steel probe tip. Note that all the peaks here also correspond to even numbered carbon species. Since only even-numbered carbon aggregates can close perfectly it is possible that the explanation for this phenomenon is that these species are fullerenes and that the larger species are giant fullerenes of the kind depicted in Figure 22.



**Figure 10.** Remarkable positive-ion laser desorption Fourier transform mass spectrum, observed by Rubin et al.<sup>45</sup> of the ring carbon oxide depicted under low laser power. This oxide which might be expected to decarbonylate to yield a  $C_{30}$  monocyclic ring has clearly dimerized to form  $C_{60}$  buckminsterfullerene!

A most exciting result was described by Rubin et al.<sup>45</sup> who have used a combination of organic synthesis and laser desorption mass spectrometry. In a preliminary study by the same group (Diederich et al.<sup>46</sup>) attempted to prepare pure carbon rings, a prominent peak for the  $C_{18}$  cluster was detected during mass spectrometric analysis of a laser desorbed 18-carbon ring precursor. This work has now been advanced in spectacular fashion; refined measurements on  $C_{18}$  and  $C_{30}$  precursors<sup>45</sup> yield mass spectra which show prominent  $C_{60}$  and  $C_{70}$  signals. However most striking is the observation that laser desorption of the  $C_{30}$  ring precursor produces a mass spectrum containing a totally dominant  $C_{60}$  signal! (Figure 10). This result suggests that, in the vapor phase, a spectacular dimerization process occurs in which two  $C_{30}$  polyyne/cumulene rings combine in a concerted folding rearrangement to form the  $C_{60}$  cage.<sup>10</sup> The implications of this process and indeed other aspects of the fullerene discovery for organic chemistry have been considered.<sup>10,61</sup>

Some of the most important of all these experiments were those of Homann and co-workers<sup>47-50</sup> who detected



**Figure 11.** Mass spectrum of  $C_{60}La$  cluster complexes and bare  $C_n$  clusters as observed by Heath et al.<sup>7</sup> when  $LaCl_3$ -doped graphite is laser vaporized (ArF 6.4 eV, 10 mJ/cm<sup>2</sup>). Note the particularly strong peak for  $C_{60}La$  and the absence of a peak for  $C_{60}La_2$ . This result is discussed in section VI (adapted from ref. 7).

$C_{60}^+$  in a sooting flame. These observations are discussed in more detail in section VII.

#### V. Stability and Intrinsic Properties of $C_{60}$

After the buckminsterfullerene structure was proposed<sup>3</sup> the intrinsic properties of the species were probed by the Rice/Sussex group.<sup>50-54</sup> It was clearly vital to determine how reliable the experimental observation of the "stability" of the  $C_{60}$  cluster was, i.e. how "special" or "magic" the cluster actually was and how certain one could be about the buckminsterfullerene hollow cage explanation. After all, the proposal appeared to rest entirely on the observation of a single, strong mass spectrum peak at 720 amu (Figures 5 and 6), and such highly circumstantial evidence needed further support. Mass spectrometry is particularly susceptible to erroneous conclusions drawn on the basis of magic numbers due to the likely presence of ionization and fragmentation artifacts. Various aspects of the original experiment led to the conclusion that the cation mass spectrum (Figures 5 and 6) was most probably an accurate reflection of the neutral cluster distribution. Nevertheless it was necessary to carry out experiments in order to probe the behavior of  $C_{60}$  more deeply in order to generate further evidence, albeit still circumstantial, to support the stability conclusion and the cage structure proposal.

During the period from 1985 to 1990 many experiments were performed by a number of groups operating in the cluster field which probed carbon behavior with a view to confirming or falsifying the fullerene-60 proposal. If  $C_{60}$  really were a cage then the most obvious next step was to attempt to trap an atom inside the cage. The first result, in this context, was the observation of  $C_{60}La$  by Heath et al.<sup>7</sup> By using a graphite disk, soaked in  $LaCl_3$  solution a strong signal was obtained for the monolanthanum complex  $C_{60}La$ , with no evidence of a peak for  $C_{60}La_2$  (Figure 11). Cox et al.<sup>51</sup> questioned the conclusion. They pointed out that, since  $C_{60}$  needs two 6.4 eV (ArF) photons for ionization and  $C_{60}La$  only one, the relative strengths of the  $C_{60}La^+$  and bare  $C_{60}^+$  MS signals should not necessarily be taken as reliable gauges of their respective abundances, and a possible  $C_{60}La_2^+$  signal might be too weak to detect.

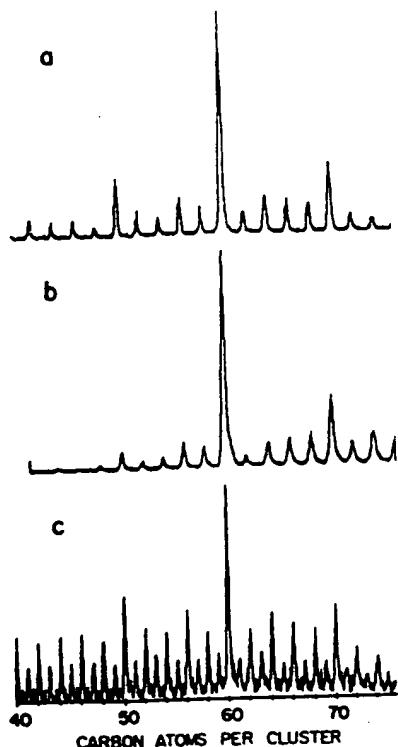
$C_{60}$ : Buckminsterfullerene

Figure 12. Carbon cluster ions observed under various production conditions.<sup>63</sup> (a) negative ions produced by directing a KrF excimer into the nozzle during expansion, (b) positive carbon cluster ions produced directly during vaporization in the nozzle without the aid of the KrF excimer laser, and (c) negative ions produced directly during vaporization in the nozzle, again without the aid of the KrF excimer laser but with longer residence time in the clustering region than in the case of the positive ions depicted in b (reprinted from ref 52; copyright 1987 Gordon and Breach Science Publishers, Inc.).

Cox et al.<sup>67</sup> have discussed further the cage hypothesis in general and metal atom encapsulation in particular and after detailed assessment they conclude that overall their observations are non-committal over whether  $C_{60}$  is a cage or not.

For the smaller carbon species the positive ions display the well known magic numbers: 11, 15, 19, 23 (the so-called " $\Delta n = 4$ " effect, cf. Figure 4) whereas the negative ions exhibit a different sequence.<sup>21-24,12</sup> The paper announcing the original discovery<sup>1</sup> assumed that the mass spectra (Figures 5 and 6) reflected accurately neutral carbon cluster distributions. If the buckminsterfullerene structural proposal were correct however, the positive and negative ion distributions would be expected to exhibit a similar prominence for the 60-carbon atom analogue. The first experiment to probe this possibility<sup>64</sup> showed that negative ions, produced by laser ionization just after the cluster beam exited from the nozzle exhibited an anion mass spectrum in which  $C_{60}^-$  was dominant. In this experiment the neutral species became negatively charged by electron transfer. If the positive or negative ions, produced directly by vaporization are studied, it is found that only after clustering is allowed to continue for a

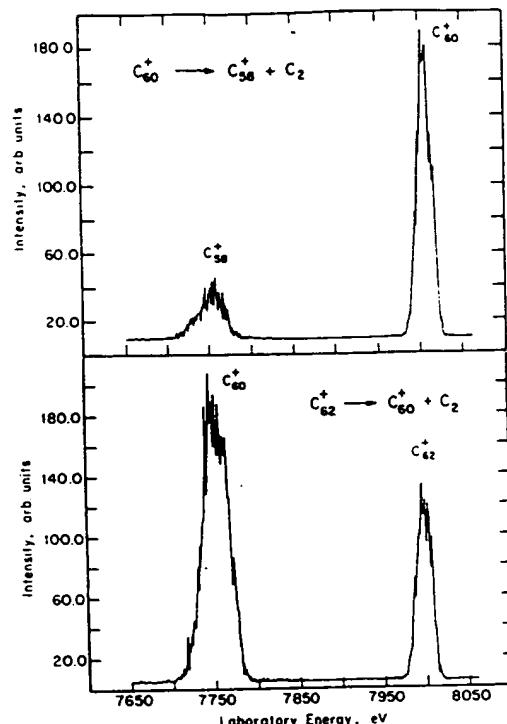
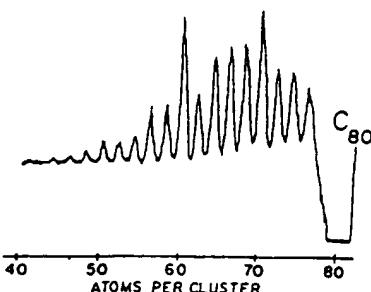


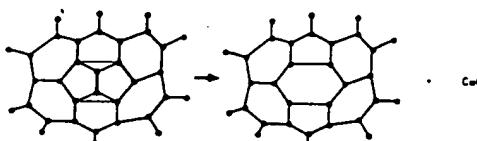
Figure 13. Metastable mass-analyzed ion kinetic energy scans (MIKES) published by Radi et al.<sup>53</sup> The parent ion (on the right) is mass selected by the magnetic analyzer and the horizontal axis is a scan of the electrostatic analyzer voltage. The parent ion energy is 8 keV.  $C_2$  loss is observed from  $C_{60}^+$  (above) and  $C_{62}^+$  (below). Note the dramatic differences in metastable activity as reflected by the relative intensities of the product peaks, relative to their parent ions in these two cases (reprinted from ref 93; copyright 1990 the American Institute of Physics).

significant length of time is the  $C_{60}^-$  anion dominant<sup>65</sup> otherwise it is not.<sup>65</sup> Some examples of mass spectra recorded under various conditions<sup>51,64,65</sup> are presented in Figure 12. Cox, Reichmann, and Kaldor<sup>67</sup> describe some intriguing relative time-of-flight differences in behavior between various individual clusters, in particular  $C_{28}$  and  $C_{60}$  which are highly dependent on the nozzle parameters. These experiments appear to suggest that wall reactions may occur in the nucleation channel. It is possible that what was observed in this experiment was  $C_{60}$  deposited in the channel which subsequently desorbed. The main evidence for the importance of wall effects lies in the detection of  $C_{60}K$  clusters when a new, pure (i.e. K free) carbon target replaces a previous one doped with potassium.

Important observations have had a bearing on the stability of  $C_{60}$ . The very early experiments by Bloomfield et al.<sup>28</sup> showed that  $C_{60}$  was susceptible to multi-photon fragmentation. A series of studies by Bowers and co-workers<sup>29-34</sup> showed that  $C_{60}$  could undergo metastable fragmentation. Particularly interesting is the observation that  $C_{60}$  exhibits much lower metastability than other neighboring clusters such as  $C_{58}$  as shown in Figure 13. These results suggest that hot  $C_{60}$  may exhibit phenomena associated with fluidity—perhaps an intriguing form of surface fluidity. On the

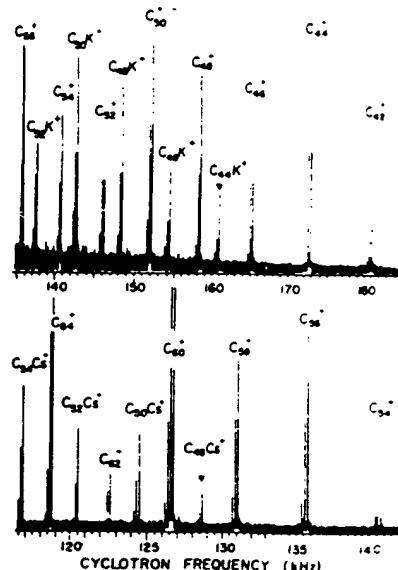


**Figure 14.** Fragmentation products under ArF (15 mJ cm<sup>-2</sup>) irradiation observed by O'Brien et al.<sup>85</sup> Under irradiation the mass selected  $C_{50}^+$  cluster (including ca. 20%  $C_{48}$  and ca. 10%  $C_{49}$ ) is here seen to fragment into smaller even clusters:  $C_{48}$ ,  $C_{46}$ , etc. by loss of  $C_2$ ,  $C_4$ , etc. Particularly interesting is the observation that  $C_{48}$  and  $C_{46}$  are favored fragmentation products (reprinted from ref 95; copyright 1988 the American Institute of Physics).



**Figure 15.** Hypothetical fragmentation-rearrangement mechanism presented by O'Brien et al.,<sup>98</sup> involving  $C_1$  loss and cage re-sealing which could explain the fragmentation phenomena in Figure 14 (reprinted from ref 95; copyright 1988 the American Institute of Physics).

other hand, O'Brien et al.<sup>25</sup> and Weiss et al.<sup>26</sup> have shown that cold  $C_{60}^+$  exhibits little, if any, evidence for fragmentation. The likely explanation for this disparity is that clusters produced under the vacuum vaporization conditions<sup>23,24</sup> possess massive amounts of internal energy leading to metastable  $C_{60}^+$ . As special behavior is most dramatic after extensive degrees of nucleation have occurred it is possible that the  $C_{60}$  signal observed under vacuum ablation conditions is actually a mixture of isomers, at least in part. Related studies by Hasselberger et al.<sup>78</sup> show that metastable fragmentation is less severe when clusters are produced with lower internal energies. The measurements of O'Brien et al.<sup>26</sup> showed that multiphoton fragmentation of clusters with 32–80 atoms occurred by elimination of even carbon fragments,  $C_n$  ( $n = 2, 4, 6, \dots$ ), rather than lower energy  $C_3$  species. Particularly intriguing is the observation that large clusters, with 70 or more atoms fragment to form smaller even-cluster distributions in which  $C_{60}$  is special (Figure 14). Clusters with less than 32 atoms fragment into a range of smaller carbon species, a result interpreted as evidence that clusters with less than 32 atoms were not cages. O'Brien et al.<sup>26</sup> also presented an interesting mechanism for this process which is depicted in Figure 15. Laser irradiation studies by Weiss et al.<sup>26</sup> showed that the metal complexes were also quite resistant to photofragmentation. They also showed that multiphoton fragmentation of  $C_{60}M^+$  resulted in metal-complex products  $C_nM^+$  for which the critical smallest sizes occur at  $n = 48, 44, 44\text{--}42$  for  $M = \text{Ca, K, and La}$ , respectively (Figure 16). This result provided strong circumstantial evidence for metal atom encapsulation because the minimum physical cage size scales with the ionic radius



**Figure 16.** High-order photofragmentation pattern of  $C_{60}K^+$  (above) and  $C_{60}Cs^+$  (below) detected by FT-ICR mass spectrometry by Weiss et al.<sup>10</sup> The break-offs observed at  $C_{60}Cs^+$  and  $C_{60}K^+$  are in excellent agreement with expectation for the smallest fullerene networks capable of encapsulating the metals, based on the known ionic radii (reprinted from ref 96; copyright 1988 American Chemical Society).

of the metals in the series.

Prior to the isolation of macroscopic samples of the fullerenes (section IX) several experiments were carried out in order to determine their physical, mainly spectroscopic, properties. Tandem TOF-MS experiments were devised to explore the possibility that the spectra of  $C_{60}$  (neutral) and  $C_{60}^+$  (the positive ion) might be responsible for the astrophysically intriguing diffuse interstellar bands (section XI). These experiments involved the resonant photodissociation of a van der Waals complex of benzene with neutral  $C_{60}$  and  $C_{60}^+$ . It proved possible to photofragment  $C_{60}C_6H_6$  but not the ion complex,  $C_{60}^+C_6H_6$ , probably because charge transfer forces bind the adduct too tightly in the ion complex.<sup>97</sup> Very weak photofragmentation of the neutral complexes of  $C_{60}$  with  $C_6H_6$  and  $CH_2Cl_2$  was observed at 3860 Å by depletion spectroscopy.<sup>98</sup>

Yang et al.<sup>10</sup> used an ingenious technique developed by Cheshnovsky et al.<sup>100</sup> to observe the UV photoelectron spectra of negative cluster ions. In these experiments the spectra of carbon clusters from  $C_{48}$  to  $C_{84}$  have been observed. Of particular interest are the UPS patterns of  $C_{50}$ ,  $C_{60}$ , and  $C_{70}$  which show a low energy LUMO feature consistent with closed shells for the neutral species.  $C_{50}$  had the lowest electron affinity: viz 2.6–2.8 eV. These observations provided further strong support for the fullerene proposal. The ionization potential of  $C_{60}$  was obtained in an elegant way by Zimmerman et al.<sup>101,102</sup> who used a series of charge transfer measurements with various reactants of known IP to bracket the IP of  $C_{60}$ :  $7.61 \pm 0.11$  eV. This result was consistent with conclusions drawn from early experiments which indicated that the IP lay between the energy of the ArF excimer laser (6.4 eV) and that of the F<sub>2</sub> laser (7.9 eV) because  $C_{60}$  was 2-photon ionized by

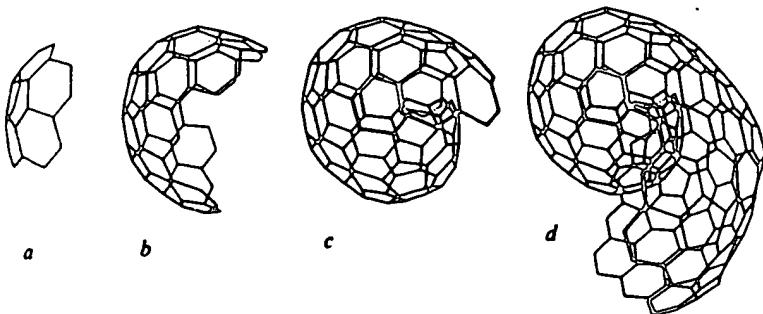
$C_{60}$ : Buckminsterfullerene

Figure 17. Diagrammatic representation<sup>102</sup> of a hypothetical carbon vapor nucleation scheme<sup>103,104</sup> proposed for the formation of concentric shell graphite microparticles. Note that the structure c has overlapped and so trapped the trailing edge inside the spiraling network. This species is thus essentially the embryo for further growth. It is proposed that  $C_{60}$  might be produced by a modification of this process in which the edges meet and seal to form a closed cage. In such a case further growth by chemical bond formation might be expected to be halted. It was conjectured that similar structures might occur as intermediates during soot nucleation (reprinted from ref 108; copyright 1988 Macmillan Magazines Ltd.).

ArF and 1-photon ionized by  $F_2$ .<sup>103,67</sup>

As mentioned in section IV, the most intriguing and convincing spectra were those obtained in the infrared study of Krätschmer, Fostiropoulos, and Huffman in 1990<sup>5,74</sup> (see further details in sections VIII and IX).

#### VI. Reaction Studies

The first reaction studies aimed at probing the cage concept were those of Heath et al.<sup>7</sup> and Cox et al.<sup>91,67</sup> (discussed in section V) who studied the carbon/metal complexes. Rohlfing et al.<sup>25</sup> and Heath et al.<sup>29,30</sup> carried out similar reaction studies which focused mainly on the properties of the carbon chains. It is also important to note that van der Waals complexes can form in the supersonic beam if  $C_{60}$  is cold.

When various gases such as CO, NO, and  $SO_2$  were introduced into a reactor, placed downstream from the nozzle in which  $C_{60}$  is formed, Zhang et al.<sup>103</sup> showed that all the even carbon clusters were totally unreactive. The odd clusters were, on the other hand, very reactive. These experiments gained significant further support from the studies of McElvany et al.<sup>70</sup> and Weiss et al.<sup>23</sup> which showed  $C_{60}$  and its analogues to be extremely unreactive in an ICR trap. However if gases are mixed with the driver gas in the nozzle, reactions can take place before and after  $C_{60}$  is formed. With hydrogen, a wide range of hydrocarbon products is detected (Rohlfing,<sup>104</sup> Hallett et al.,<sup>103</sup> and Doverstal et al.<sup>103</sup>). Rohlfing has used an in-line reflection modification of the cluster beam technique and made some very careful high-resolution mass spectrometric measurements of the reactions of clusters  $C_{20}$ – $C_{60}$  with hydrogen.<sup>104</sup> The variations in reactivity appear to be structure related and consistent with the cage proposal. The study suggests that chain cluster species with as many as 44 carbon atoms may be present. Complementary experiments by Hallett et al.<sup>103</sup> and Doverstal et al.<sup>103</sup> indicate that clusters in the  $C_{20}$ – $C_{60}$  range show at least three different types of reactivity as evidenced by the mass spectrometric patterns of the hydrogenated products. The observations<sup>103</sup> are consistent with the proposal that small fullerenes ( $C_{20}$ ,  $C_{24}$ ,  $C_{28}$ ,  $C_{32}$ ,  $C_{60}$ ) can form.<sup>6</sup> They are also consistent with the fact that formation that no 22 atom fullerene can exist, as

#### VII. Gas-Phase Carbon Nucleation and $C_{60}$ Formation

It would appear that most workers in the field are able to observe special behavior fairly easily and under a wide range of conditions, all of which have one major feature in common:  $C_{60}$  appears to be dominant only when nucleation nears completion, leaving behind  $C_{60}$  and other even-numbered relatives such as  $C_{70}$ . This result has one obviously simple explanation; at least some fraction of the even clusters—particularly  $C_{60}$ —is unreactive toward growth into macroscopic particles. The spontaneous creation of  $C_{60}$  requires a mechanistic explanation. In particular, entropy factors clearly need to be carefully assessed when it is proposed that so symmetric an object is formed in a chaotic plasma. A feasible nucleation mechanism was provided by Zhang et al.<sup>103</sup> and refined further by Kroto and McKay.<sup>102</sup> The nucleation model proposes that curved  $sp^2$ -linked (aromatic) carbon networks form (Figure 17) and can serve as embryos for further growth. The energetics of sheet carbon cluster radicals is invoked to explain the curvature/partial closure. Essentially the drive toward closure is governed by the energy released as a result of eliminating the edge dangling bonds. For instance a flat graphite-like sheet of 60 atoms would have at least 20 dangling bonds, whereas fullerene-60 would, of course, have none. In general, in a chaotic system, partly closed, overlapped embryos, such as that shown in Figure 16c, are expected to form and which, once overlapped, cannot close perfectly. These species are probably highly active nucleation sites to which permanent chemical binding of adsorbing fragments can take place. Of course some form of closure/annealing process might take place if the temperature is high enough for intra and extra network rearrangement to occur. It was proposed<sup>102,103</sup> that during this general spiral nucleation process some embryos would close forming fullerenes, particularly fullerene-60 which would no longer present a site for efficient accretion. The process is primarily a physicochemical nucleation scheme in which the fullerenes act as deadends for the most rapid nucleation.

After embryo formation, epitaxial growth has been shown to result in icospiral graphitic giant molecules or micronartiles<sup>103</sup> with structures consistent with

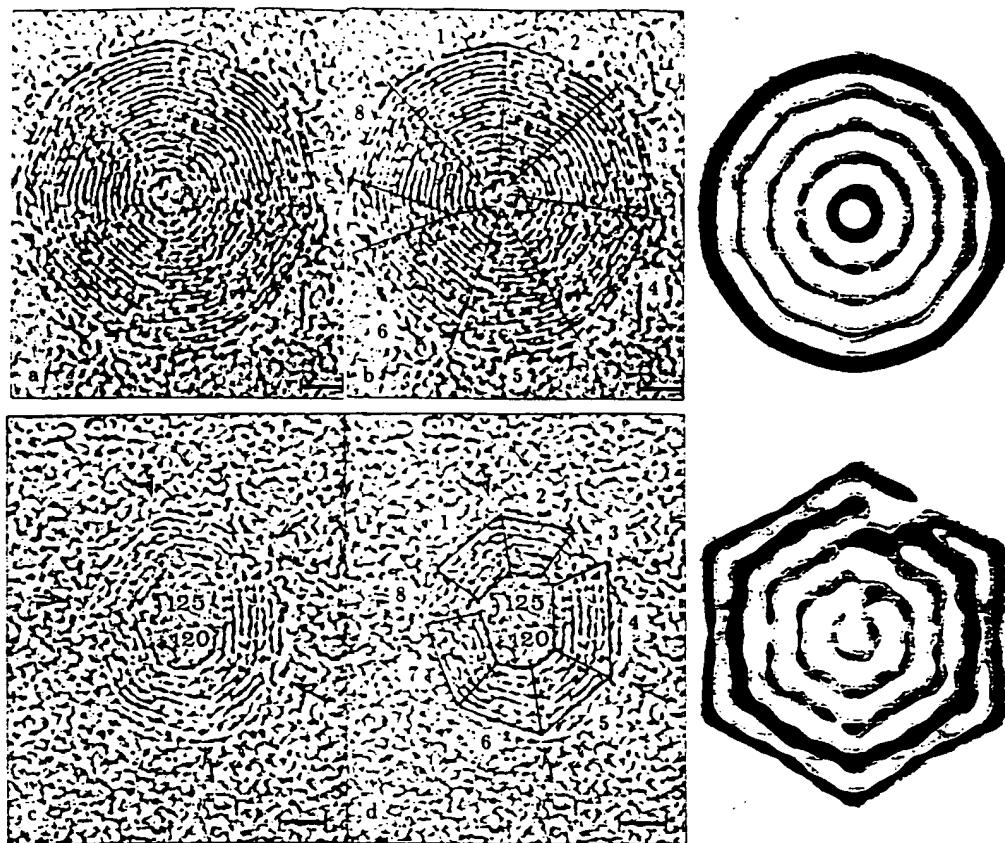


Figure 18. Comparison by McKay et al.<sup>111,112</sup> between TEM images of polyhedral graphitic microparticles observed by Iijima<sup>109</sup> and simulated TEM images for a hypothetical spiral shell particle predicted by the nucleation scheme depicted in Figure 17. The fairly round particle observed by Iijima which is depicted in a and b is seen to exhibit a similar pattern to the simulation top right. On the other hand the more polygonal particle, shown in c and d, exhibits a similar pattern to the simulation shown bottom right. The simulations are for the same particle observed from different angles. The hypothetical particle has shell interconnections which can most easily be seen in the lower right simulation. In b and d the polygonal outlines are delineated.

those of spheroidal graphitic microparticles observed by Iijima in 1980.<sup>109,110</sup> Kroto et al.<sup>111,112</sup> have provided further support for the scheme in the form of TEM image simulations based on theicosahedral concentric shell structure concept,<sup>108</sup> in excellent agreement with the Iijima images as depicted in Figure 18. Roulston et al.<sup>113</sup> have shown that certain electronic and structural properties of amorphous semiconducting carbons can be explained on the basis of a spheroidal graphitic infrastructure, rather than by the traditional flat microstructure. Yacaman et al.<sup>114,115</sup> have shown that FT power-spectra processed, electron microscope images of carbon microparticles appear to be consistent with the quasicosahedral spiral substructure.<sup>108</sup> Attention has been drawn to the fact that small graphitic microparticles actually consist of crystalline quasicosahedral graphitic cores surrounded by amorphous carbon surface layers.<sup>116,117</sup> Interestingly, Iijima<sup>110</sup> has shown that the TEM structure at the nucleus of one of the carbon microparticles, studied earlier<sup>109</sup> was consistent with the image expected if it were a  $C_{60}$  cage. With hindsight this result demands further serious investigation to see whether fullerene-60 can itself be encapsulated during

later stages of particle growth.

Wales<sup>117</sup> has considered some statistical aspects of the growth dynamics of closed-cage structures and Bernholc and Phillips have discussed the kinetic factors involved in the growth of carbon clusters in general.<sup>118</sup>

It was also suggested that a modified form of the nucleation scheme, devised to account for the spontaneous creation of  $C_{60}$ , could also explain the spheroidal nature of soot.<sup>109,110,116,119</sup> This proposal was criticized by Frenklach, Ebert, and co-workers<sup>120-123</sup> who favor an earlier theory, which invokes the physical condensation of flat PAH molecules held together by van der Waals forces into coagulating liquid drops. However, Harris and Weiner point out how little has been firmly established about the soot formation mechanism.<sup>124</sup> It can in fact be demonstrated<sup>125</sup> that the new scheme is broadly consistent with kinetic, structural, and chemical observations made on soot and its formation process.

The new nucleation scheme predicts that some  $C_{60}$  should form as a byproduct<sup>108,109</sup> of soot production. Subsequently Gerhardt, Löffler and Homann,<sup>87-90</sup> in studies of the ions produced in a sooting flame, found conditions under which the mass spectrum shown in

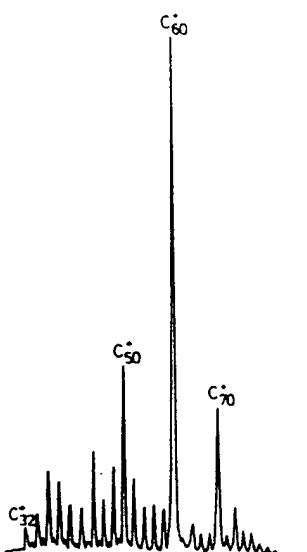


Figure 19. Mass spectrum, observed by Gerhardt, Löffler, and Homann,<sup>87-90</sup> of positive ions produced by a sooting benzene/oxygen flame (C/O = 0.76) (reprinted from ref 87; copyright 1987 Elsevier Science Publishers).

Figure 19 is obtained. This spectrum is almost identical with that observed during the pure carbon laser vaporization experiments where  $C_{60}^+$  is the dominant ion! Homann and co-workers conclude that this observation should not be taken as support for the new spiral nucleation scenario as the tell-tale even ions with a dominant  $C_{60}^+$  peak are not seen until after the inception of soot particle formation. The carbon/hydrogen reaction studies<sup>104-106</sup> promise to shed further light on the soot formation process, but the way in which the results might dovetail with the conventional data remains to be ascertained. Kroto has summarized the present state of affairs from this viewpoint.<sup>125</sup>

#### VIII. Theoretical Studies of the Fullerenes

Theoretical studies predating the discovery of  $C_{60}$  have been discussed in section II. After the discovery, theoreticians had a ball and many aspects of the molecule's properties have already been probed. The comprehensive overview of theoretical work on fullerene-60 presented by Weltner and Van Zee<sup>2</sup> is here conflated with more recent work.

One important aspect of the original experimental observations was the fact that  $C_{70}$  also showed special

behavior. Topological and chemical stability arguments, as discussed by Kroto<sup>8</sup> and Schmalz et al.,<sup>9</sup> explain this observation as being entirely consistent with the fullerene proposal. Indeed these studies suggested that if the  $C_{60}$  mass spectrometric signal were due to its having a closed cage fullerene structure,  $C_{70}$  should show special behavior also, for the same reason. Thus, most importantly and rather convincingly, the fullerene structure proposal no longer rested on the single line observation. In fact it had now gained significant further support by the fact that a prediction had been made and neatly confirmed. Indeed the two observations, taken together, provided convincing evidence for the existence of a whole family of fullerenes and further probing suggested that in addition to  $C_{60}$  and  $C_{70}$ , the  $C_{24}$ ,  $C_{28}$ ,  $C_{32}$ , and  $C_{50}$  clusters (Figure 20) should also show varying degrees of special stability<sup>8,9</sup> (N.B. fullerene-22 cannot exist<sup>107</sup>).

The dominance of  $C_{60}$  and  $C_{70}$  was ascribed to the fact that these are the smallest fullerenes that can have an isomer (one in each case) in which none of the 12 pentagonal configurations, necessary and sufficient for closure, abut.<sup>8,9</sup> It was shown<sup>8,9</sup> that the predictions were commensurate with the mass spectrum obtained by Cox et al.<sup>67</sup> (Figure 21) and consequently there existed convincing experimental evidence for the fullerene family proposal. Since even-numbered carbon clusters are detectable with as many as 600 or more carbon atoms,<sup>84</sup> the possibility of giant fullerenes<sup>108,126</sup> such as  $C_{240}$  and  $C_{540}$  shown in Figure 22 appears to be an exciting possibility.<sup>60</sup>

Isomer stability has been discussed by Stone and Wales<sup>127</sup> who noted that the difference in energy between isomers is small and suggested that the  $C_{60}$  signal should be due to a mixture of isomers. This result is difficult to reconcile with the observation (Figures 5 and 6) since it leads to the conclusion that  $C_{60}$  is no more special than other clusters such as  $C_{62}$ . Potential energy functions have now been developed for the carbon cages systems by Takai et al.<sup>128</sup> and Balm et al.<sup>129</sup> The simulated annealing, Monte-Carlo methods used by Zerbetto<sup>130</sup> to study the behavior of small carbon clusters have been applied by Ballone and Milani<sup>131</sup> in order to show that the fullerene cages are minimum energy structures.

A group theoretical analysis of the electronic properties of the fullerene family, by Fowler and Steer,<sup>107</sup> showed that the members,  $C_n$  where  $n = 60 + 6k$  ( $k = 0, 1, 2, 3, 4, \dots$ , i.e. an integer other than one), should have closed-shell electronic structures. The degree of aromaticity in a compound is of interest, and the number of Kekulé structures is often considered to be a guide. A total of 12500 for fullerene-60 has been calculated

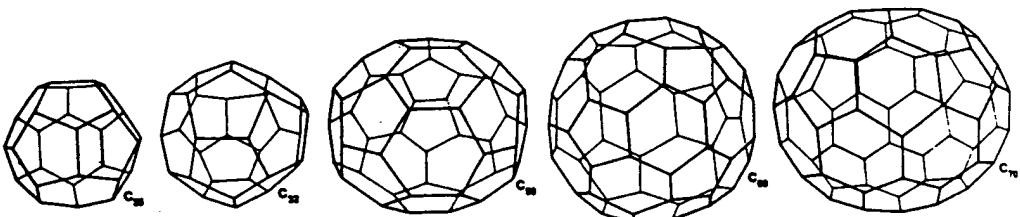


Figure 20. Five possible "magic" fullerenes predicted to display enhanced stability, relative to others in the range with 20-80 atoms, on the basis of chemical and synthetic factors (reprinted from ref 8. Copyright 1987 Macmillan Materials Ltd).

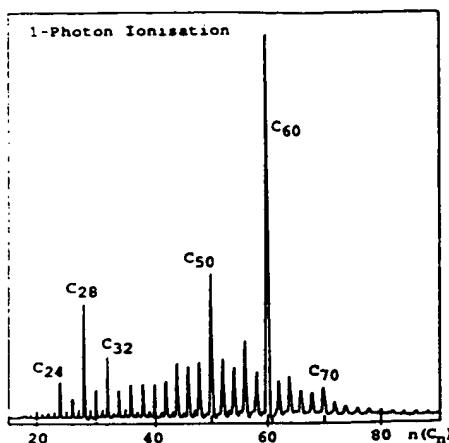


Figure 21. Time-of-flight mass spectrum taken from the data of Cox, Reichmann, and Kaldor.<sup>67</sup> The strong peaks are in excellent agreement with expectation<sup>49</sup> if they correspond to fullerenes. The fullerenes 24, 28, 32, 50, 60, and 70 (Figure 20) are predicted to exhibit enhanced stability, i.e. are magic. Note the sharp cutoff at C<sub>24</sub> which is consistent with the fact that a no 22 atom fullerene can form.

by Schmalz et al.,<sup>132</sup> Hosoya,<sup>133</sup> Brendsdal and Cyvin,<sup>134</sup> and by Elser.<sup>135</sup> Resonance circuit theory has been applied to this problem by Schmalz et al.,<sup>132,9</sup> Klein et al.,<sup>136,137</sup> as well as Randic, Nikolic, and Trinajstic.<sup>138-140</sup> These studies indicate that account must be taken of the fact that some resonance structures make negative contributions to the aromatic stabilization. Schmalz et al.<sup>9</sup> compared resonance circuit theory with Hückel molecular orbital (HMO) theory and concluded that C<sub>60</sub> should be less aromatic than benzene. Amic and Trinajstic<sup>140</sup> discuss stabilization arising from bond delocalization. Graph theory has been applied to C<sub>60</sub> and to other systems by Balasubramanian and Liu<sup>141,142</sup> and also by Dias who has circumvented group theory in order to simplify Hückel calculations.<sup>143</sup> Hückel calculations on fullerene-60 have been made by Haymet<sup>144,20</sup> and the stabilization due to delocalization discussed. Jiang and Zhang<sup>145</sup> have calculated the stability of fullerene-60 by Hückel theory using moment analysis techniques. Hess and Schaad<sup>146</sup> as well as

Aihara and Hosoya<sup>147</sup> have also applied Hückel theory to the problem, focusing on aspects of spheroidal aromaticity.

Fowler and Woolrich<sup>148</sup> have made three-dimensional HMO calculations which predict that C<sub>60</sub> and C<sub>70</sub> are closed shell systems. Fowler<sup>149</sup> extended this approach in order to assess the stability in other, larger fullerene cages, while Fowler, Cremona, and Steer<sup>150</sup> have discussed bonding in nonicosahedral spheroidal fullerene cages. Fowler<sup>151</sup> has extended these ideas to various classes of cylindrical fullerenes and predicted closed electronic shells with an empty nonbonding orbital for clusters consisting of 10(7 + 3k) and 12(7 + 3k) atoms with 5- and 6-fold symmetry. Ceulemans and Fowler<sup>152,153</sup> considered possible Jahn-Teller distortion pathways for icosahedral molecules.

Bvers Brown<sup>154</sup> has discussed the simplification that high symmetry imparts to  $\pi$ -system calculations and obtained algebraic solutions for the orbital energies of fullerene-60. Electronic and vibrational properties were calculated by using a two-dimensional HMO method by Coulombeau and Rassat.<sup>155</sup> Semiempirical calculations including the effects of nonplanar  $\pi$ -orbital overlap due to curvature have also been carried out by using the free-electron model in the Coulson-Golubiewski, self-consistent Hückel approximation by Ozaki and Takahashi.<sup>156</sup> Haddon et al.<sup>157,158</sup> have also considered the effects of nonplanarity, i.e. pyramidalization.

Extended Hückel calculations by Bochvar, Gal'pern, and Stankovich<sup>159</sup> and INDO and INDO/CI calculations by Feng et al.<sup>160</sup> have been applied to C<sub>60</sub> and its isomers. A comparison between C<sub>60</sub> and graphite was made by MNDO with geometry optimization by Newton and Stanton.<sup>161</sup> McKee and Herndon<sup>162</sup> also applied MNDO theory to cage carbons and concluded that the flat "graphitene" cage,<sup>144</sup> in which two coronene sheets are linked by pentagonal rings at the edge to form a disk-like structure should be more stable than fullerene-60. These authors also considered the mechanism of formation arising from rearrangement. Rehybridization and bonding were studied by Haddon, Brus, and Raghavachari who applied the  $\pi$ -orbital axis vector/3d-HMO (POAV/3D HMO) method<sup>157,158</sup> and concluded that larger clusters were favored. It was also postulated that fullerene-240 should be more stable than C<sub>60</sub>. Lüthi and Almlöf<sup>163-165</sup> have carried out

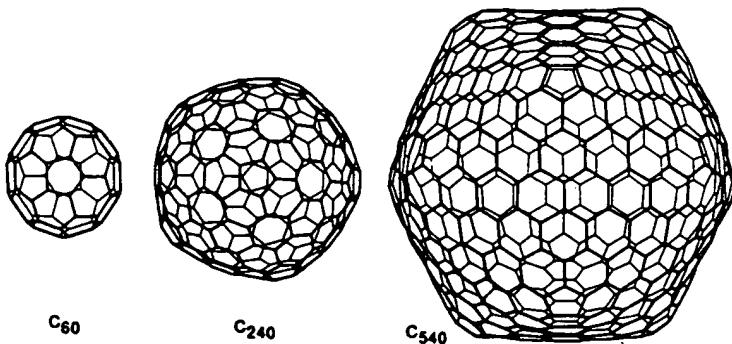


Figure 22. The set of fullerenes C<sub>60</sub>, C<sub>240</sub>, and C<sub>540</sub> with diameters in the ratio 1:2:3. Kroto and McKay<sup>108</sup> showed that quasiicosahedral shape develops rapidly for the giant fullerenes. Strain in the giant fullerenes is expected to be focused in the regions of the coronulene-like cusps. The surface thus becomes a smoothly curving network connecting the twelve cusps (reprinted from ref 108; copyright 1988 Macmillan Magazines Ltd.).

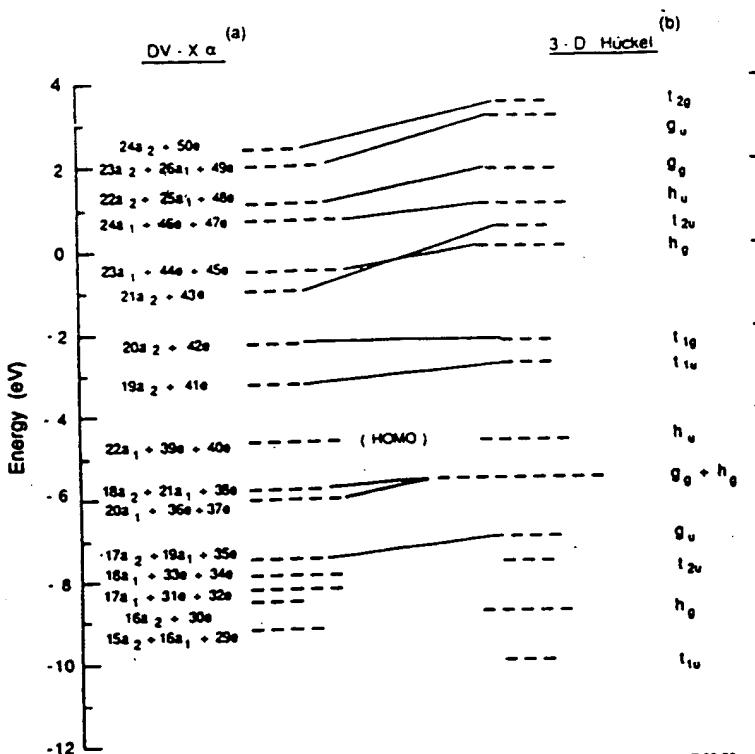


Figure 23. Orbital energy level diagram for fullerene-60 presented by Hale.<sup>169</sup> The energies derived by DV-X $\alpha$  calculations assuming  $D_5$  symmetry on the left are compared with Hückel results. In the diagram  $\beta$  has been given the value -2.52 eV (reprinted from ref 169; copyright 1986 American Chemical Society).

large-scale restricted Hartree-Fock calculations and they deduced that  $\Delta H_f = 415-490$  kcal/mol (relative to graphite) the electron affinity should be 0.8 eV and the ionization energy 7.92 eV. The electron affinity (2.4 eV) has been calculated by Larsson, Volosov, and Rosen<sup>166</sup> and by Braga et al.<sup>167</sup> Schulman and Disch<sup>168</sup> have calculated the heat of formation on the basis of ab initio SCF theory.

Hale<sup>169</sup> determined electronic properties, such as the ionization energy for fullerene-60, by the discrete variational (DV)-X $\alpha$  method using the Slater transition state formalism. Such calculations tend to be good for spheroidal systems. Hale's orbital energy level diagram for fullerene-60 is reproduced in Figure 23. The linear combination of muffin-tin orbital method in its atomic sphere approximation (LMTO ASA) was applied by Satpathy.<sup>170</sup> Calculations in which the partial retention of differential overlap PRDDO approach was applied were carried out by Marynick and Estreicher.<sup>171</sup> Stone's tensor surface harmonic theory was used by Fowler and Woolrich.<sup>168</sup> The IMOA method (iterative maximum overlap approximation) was applied to a range of fullerenes by Kovacević, Graovac, and Babic<sup>172</sup> to assess hybridization, structure and the amount of strain in these cages. Haddon<sup>173</sup> has discussed degree of pyramidalization considerations for fullerene-60 and other aromatic compounds.

Fahre and Rassat have reviewed the properties of known aromatic molecules which are essentially com-

In some of the calculations the electronic spectra of the fullerenes were the main focus. The calculations of Kataoka and Nakajima<sup>174</sup> and László and Udvárdi<sup>175</sup> used the Pariser-Parr-Pople method (with CI) to determine spectra, structural parameters, and oscillator strengths. Optimized INDO calculations were published by Shibuya and Yoshitani.<sup>177</sup> The electronic structure and the spectra have also been studied by the CNDO/S method (including CI) by Larsson et al.<sup>166</sup> and by Braga et al.<sup>167</sup> Hayden and Mele<sup>178</sup> evaluated  $\pi$ -bonding behavior using the tight-binding model with electron-phonon coupling for the ground and excited states of fullerene-60. Jahn-Teller instabilities in the excited electronic states and the ion have been classified by Negri, Orlandi, and Zerbetto<sup>179</sup> who have also estimated Franck-Condon patterns and phosphorescence quantum yields.

Several calculations focused on the vibrational properties of fullerene-60. The result of primary (and historical) significance is that only four fundamentals are IR active due to the high symmetry of the molecule. Of the 174 vibrational modes giving rise to 42 fundamentals of various symmetries, four have  $t_{1g}$  symmetry and are IR active whereas 10 (eight  $h_g$  and two  $a_g$ ) are Raman active.

Newton and Stanton<sup>181</sup> gave preliminary details of the vibrational behavior of fullerene-60 using MNDO theory. A non-Cartesian coordinate method was employed to describe the C<sub>60</sub> vibrations in terms of four-force field constants by Wu, Iakobi, and Garrett<sup>180</sup> A *ab initio*

SCF/STO-3G calculations of the vibrational properties of  $C_{60}$  and other symmetric carbon cages have been published by Disch and Schulman.<sup>181</sup> Schulman et al.<sup>182</sup> have applied the ab initio and AM1 methods to fullerene-24 and fullerene-60 in order to obtain heats of formation, vibrational frequencies, and ionization energies. Coulombeau and Rassat have considered the vibrations of several fullerenes up to fullerene-120.<sup>183</sup> They have also discussed hydrofullerenes.<sup>184</sup> In addition to calculating the rotational properties on the basis of icosahedral symmetry analysis,<sup>184</sup> Weeks and Harter have carried out a normal mode study on the basis of a classical spring/mass model.<sup>185</sup> They have also discussed the rovibrational properties of fullerene-60.<sup>185-189</sup> Stanton and Newton<sup>190</sup> extended and revised earlier MNDO studies giving detailed information on the normal modes. They have derived group theory invariance theorems for vibrational analysis and have discussed the  $A_g$  vibration which essentially consists of rotary oscillations of the pentagonal rings. Cyvin et al.<sup>191</sup> used a 5-parameter force field to calculate the frequencies of the four IR active and 10 Raman-active modes; and Brendsdal et al.<sup>192</sup> have considered approximate methods in order to determine all 46 vibrational frequencies. Brendsdal<sup>193</sup> has discussed the symmetry coordinates.

Slanina et al. have carried out a harmonic vibrational analysis within the AM1 method for fullerene-60 and also fullerene-70.<sup>194</sup> The study has been extended to include consideration of structural, energetic, and thermodynamic properties of both species using MMP2 and MNDO methods.<sup>195-197</sup> Bakowies and Thiel<sup>198,199</sup> have used the MNDO approach to calculate the IR spectra of a whole range of fullerenes from  $C_{24}$ - $C_{240}$ . For  $C_{70}$  they deduce that one vibrational band should be significantly more intense than the rest, see section X.

Heymann has discussed the possibility that He may be trapped in a fullerene-60 cage.<sup>200</sup> Calculations have been made of the spectroscopic properties of various intracage complexes by Ballester et al.<sup>201</sup> assuming the central atom is trapped in a polarizable uniform (spherical) dielectric cage. Kroto and Jura<sup>202</sup> have discussed the importance of charge-transfer processes in the spectra of neutral and ionic fullerene intra- as well as extracage (van der Waals) complexes. For the ions the energy is just the difference between the ionization potentials of the  $C_{60}$  cage and the encapsulated species. Van der Waals complexes such as  $C_{60}H^+$  are likely to be particularly important (section XI). Rosen and Waestberg have calculated the electronic structure of  $C_{60}La$  (and  $C_{60}$ ) obtaining ionization energies and electron affinities for the neutral and ionic species within the local-density approximation.<sup>203,204</sup> Saito<sup>205</sup> has also used the local density approximation to calculate the electronic properties of  $C_{60}M$  ( $M = K, O, Cl$ ).

Theoretical calculations have been carried out on fullerene-60 derivatives such as hydrofullerenes by Coulombeau and Rassat<sup>184</sup> and by Scuseria<sup>206</sup> who has also considered the perfluorofullerene,  $C_{60}F_{60}$ . Crystal packing considerations for spheroidal molecules including fullerene-60, have been discussed by Williams.<sup>207</sup>

Several papers have focused on the likely electrical and/or magnetic properties of the fullerenes in particular fullerene-60. Klein and Haddon<sup>208,209</sup> using LMMO

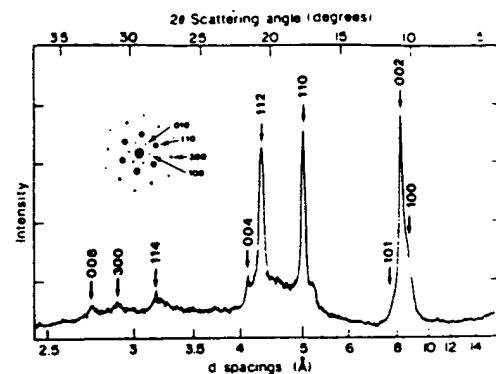


Figure 24. X-ray diffraction pattern of a microcrystalline powder of fullerene-60 obtained by Krätschmer, Lamb, Fostiropoulos, and Huffman.<sup>4</sup> Inset (upper left) is a single-crystal electron diffraction pattern (shown in more detail in Figure 25) indexed with Miller indices compatible with the X-ray pattern. This pattern provided unequivocal evidence that the  $C_{60}$  species they had isolated was a round ball 10 Å in diameter in perfect agreement with expectation for buckminsterfullerene (reprinted from ref 4; copyright 1990 Macmillan Magazines Ltd.).

and London theory, calculated the ring current magnetic susceptibility and concluded that the shielding should be vanishingly small (less than 1 ppm) due to cancellation of the diamagnetic and paramagnetic contributions. They concluded that fullerene-60 should not show normal aromatic behavior. Studies by Fowler, Lazzaretti, and Zanasi<sup>210</sup> and Pauling<sup>211</sup> have suggested however that the diamagnetic term has been underestimated. From large scale ab initio, coupled Hartree-Fock calculations (involving all electrons) of the polarizability and magnetizability of  $C_{60}$  and  $C_{20}^{2+}$ , Fowler et al.<sup>210</sup> conclude that the shielding should be roughly the same as for related aromatic systems. Haddon and Elser<sup>212</sup> have discussed their own results<sup>208,209</sup> and reinterpreted those of Fowler et al.<sup>210</sup> and conclude that the latter study is consistent with a small delocalized susceptibility. Schmalz<sup>213</sup> has argued that the Fowler et al.<sup>210</sup> interpretation is correct. The NMR study of Taylor et al.<sup>6</sup> yielded a chemical shift for fullerene-60 which is fairly typical for an aromatic species. Fowler et al.<sup>214</sup> have extended their approach to the calculation of the shifts in fullerene-70, obtaining results consistent with observation and confirming the line assignments made by Taylor et al.<sup>6</sup> This problem is further discussed in section X.

#### IX. The Isolation, Separation, and Structural Characterization of Fullerenes-60 and -70

Almost five years, to the day, since the special behavior of the  $C_{60}$  signal was recognized (Figure 5) and the buckminsterfullerene proposal made,<sup>3</sup> macroscopic samples were isolated and characterized. Krätschmer, Lamb, Fostiropoulos, and Huffman,<sup>4</sup> in following up their earlier IR observations,<sup>5,74</sup> discovered that at ca. 300–400 °C a solid material could be sublimed from the deposit obtained from arc-processed graphite. They found that this sublimate was soluble in benzene and could be crystallized. The X-ray and electron diffraction analyses (Figures 24 and 25) of the crystalline material so obtained (Figure 26) showed it consisted of

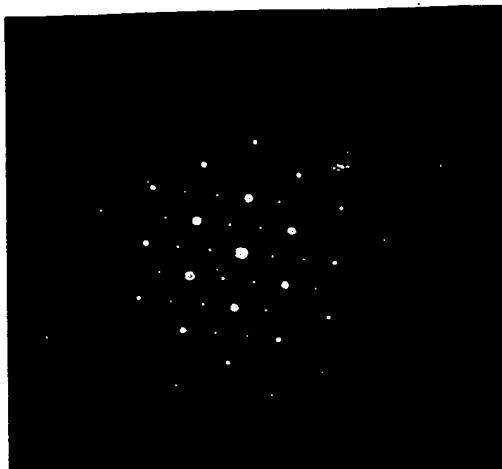


Figure 25. Single-crystal electron diffraction pattern of fullerene-60.<sup>4</sup> Further details of indices are given in Figure 24 (reprinted from ref 4; copyright 1990 Macmillan Magazines Ltd.).

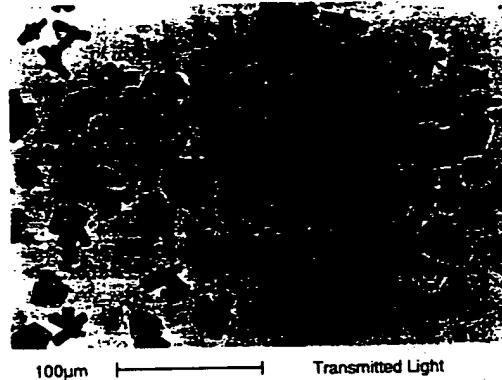


Figure 26. Transmission micrograph of crystals extracted by Krätschmer et al.<sup>4</sup> from the deposit of arc-processed graphite. Thin platelets, rods and stars of hexagonal symmetry are observed (reprinted from ref 4; copyright 1990 Macmillan Magazines Ltd.).

by ca. 3.1 Å (in graphite the interlayer distance is 3.4–3.5 Å). These authors also reported IR (Figure 27), UV/vis, and mass spectra of the extracted material. Bands of C<sub>70</sub> were present (weakly) in the IR spectrum and, in the UV/vis spectrum, some features of fullerene-60 were masked by those of fullerene-70. These results provided the first confirmation of the fullerene-60 structural proposal.

In a parallel and independent study of similarly arc-processed carbon, Taylor et al.<sup>6</sup> had also shown that C<sub>60</sub> was present by FAB-sampled mass spectrometry and that a red soluble extract could be obtained by treating the carbon deposit directly with benzene. Taylor et al.<sup>6</sup> processed the extract by the Soxhlet procedure and obtained a material which mass spectrometry showed to contain a range of fullerenes, C<sub>60</sub> and C<sub>70</sub> in particular (Figure 28). This material was chromatographed by using hexane/alumina, and C<sub>60</sub> and C<sub>70</sub> were thereby separated into a magenta and red fractions, respectively. <sup>13</sup>C NMR measurements yielded a single line for C<sub>60</sub> (Diameter 90 Å) providing definitive

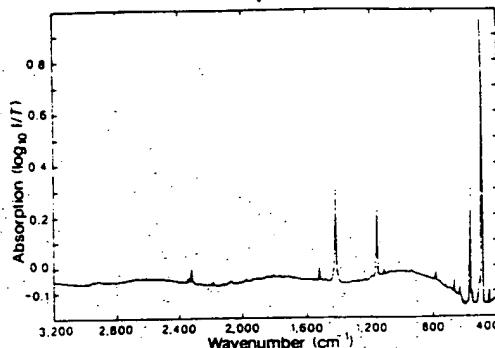


Figure 27. Infrared spectrum of fullerene-60 presented by Krätschmer et al.<sup>4</sup> showing the four fundamentals in excellent agreement with expectation for the proposed fullerene-60 structure. Weaker features belong to fullerene-70 (reprinted from ref 4; copyright 1990 Macmillan Magazines Ltd.).

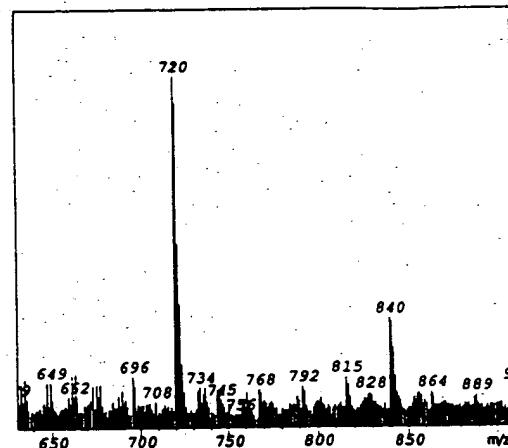


Figure 28. FAB-sampled mass spectrum, obtained by Taylor et al.<sup>6</sup> of the soluble material extracted from arc-processed graphite. Apart from unequivocal evidence for C<sub>60</sub> and C<sub>70</sub> in the extract there is also evidence for other even-numbered carbon species, particularly C<sub>50</sub> and C<sub>80</sub> (reprinted from ref 6; copyright 1990 The Royal Society of Chemistry).

proof that all 60 atoms are equivalent—a result totally commensurate with the buckminsterfullerene structure. There is of course the alternative solution that all the atoms are located on the perimeter of a monocyclic ring. This (explosively) unlikely possibility was eliminated by the NMR spectrum of C<sub>70</sub> which consisted of a set of five lines (Figure 29c) with a chemical shift pattern and relative intensities commensurate with the fullerene-70 structure (Figure 30b) first suggested by Heath et al.<sup>7</sup> This result not only confirmed the fullerene 5/6-ring geodesic topology but also eliminated the possibility that the carbon atoms might be fluxional. Almost as important is the confirmation, by this result, of the existence of other members of the fullerene family.

#### X. Postbuckminsterfullerene Research—The First Results

Since the revelation that macroscopic samples of the fullerenes can be isolated and that they are soluble and

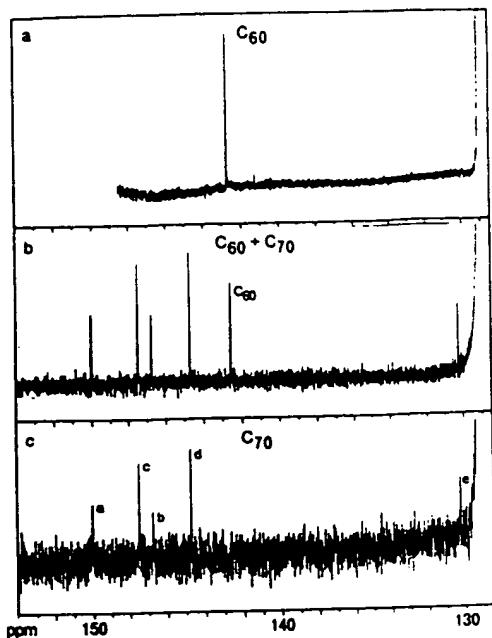


Figure 29.  $^{13}\text{C}$  NMR spectra obtained from chromatographically purified samples (Taylor et al.<sup>9</sup>) of soluble material extracted from arc-processed graphite: (a)  $^{13}\text{C}$  NMR spectrum of a purified sample exhibiting only a single resonance, (b) spectrum of a mixed sample, and (c) spectrum of a purified sample of  $\text{C}_{70}$  from which  $\text{C}_{60}$  has been eliminated. These spectra are consistent with the structures and assignments presented in Figure 20. The wing of the intense benzene solvent signal lies to the far right-hand side. This set of observations provided unequivocal evidence that the carbon atoms in  $\text{C}_{60}$  were indeed all equivalent in perfect agreement with expectation if the molecule were buckminsterfullerene (Figure 30). The five-line spectrum for  $\text{C}_{70}$  is also totally consistent with that expected for  $(\text{D}_{3h})\text{fullerene-70}$  (Figure 30). This spectrum eliminated any lingering doubt there might have been that the C atoms were either fluxional or perhaps located on the perimeter of a monocyclic ring. It also provided evidence for the stability of other members of fullerene family<sup>1-6</sup> (reprinted from ref 6; copyright 1990 The Royal Society of Chemistry).

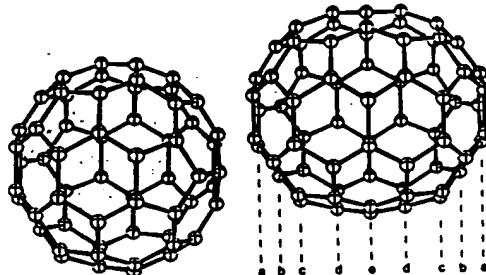


Figure 30. Schematic diagrams of fullerene-60 and fullerene-70 (based on diagrams of Slanina et al.<sup>124</sup>). All sixty atoms in fullerene-60 are equivalent whereas fullerene-70 possesses five different types of carbon in the ratios 10:10:20:20:10 in the order a:b:c:d:e respectively as shown. Compare with the NMR spectrum shown in Figure 29.

chromatographically separable, it is now the turn of experimentalist to have a ball. Ajie et al.<sup>215</sup> and Hare et al.<sup>216</sup> have observed the UV-visible spectra of chromatographically separated fullerene-60 and fullerene-70<sup>216</sup> in hexane solution (reprinted from ref 216; copyright 1991 Elsevier Science Publishers).

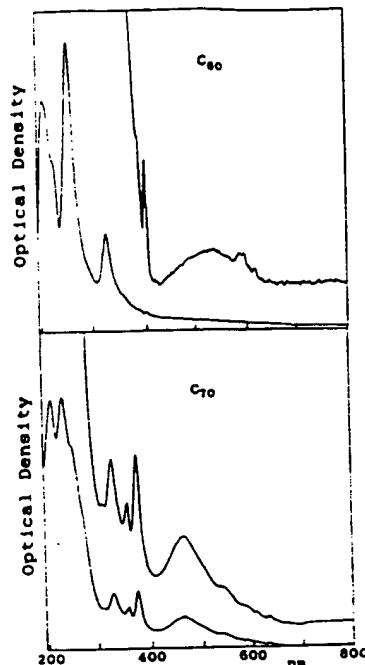


Figure 31. UV-vis spectra of chromatographically separated fullerene-60 and fullerene-70<sup>216</sup> in hexane solution (reprinted from ref 216; copyright 1991 Elsevier Science Publishers).

TABLE I. Properties of  $\text{C}_{60}$  Buckminsterfullerene

| Vibrational Frequencies |                      |                                     |
|-------------------------|----------------------|-------------------------------------|
| abs(obs) <sup>a</sup>   | em(obs) <sup>b</sup> | calc. $\text{cm}^{-1}$ <sup>c</sup> |
| 528                     | 527.1                | 472                                 |
| 577                     | 570.3                | 618                                 |
| 1183                    | 1169.1               | 1119                                |
| 1429                    | 1406.9               | 1434                                |

| X-ray Data <sup>d</sup>              |                      |
|--------------------------------------|----------------------|
| $r(\text{C}-\text{C}) = 1.388$ (9) Å | six-six ring fusion  |
| $r(\text{C}-\text{C}) = 1.432$ (5) Å | five-six ring fusion |

| NMR Data <sup>e</sup>         |            |
|-------------------------------|------------|
| chemical shift (benzene soln) | 142.68 ppm |

| Electronic/Spectroscopic Data  |  |
|--------------------------------|--|
| electron affinity <sup>f</sup> | 2.6-2.8 eV   |
| ionization energy <sup>g</sup> | 7.61 (0.02) eV   |
| UV-vis bands <sup>h</sup>      | 213, 257, 329 ( $\epsilon_{\text{max}} = 135\,000, 175\,000, 51\,000$ )<br>404 (w) 440-670 (brd) (max. 500, 540, 570, 600, 625) nm |

<sup>a</sup> Reference 4. <sup>b</sup> Reference 218. <sup>c</sup> Reference 191. <sup>d</sup> Reference 222. <sup>e</sup> See also Figures 24, 32, and 34. <sup>f</sup> See Figure 28. <sup>g</sup> Reference 6 (see also refs 215 and 228). <sup>h</sup> Reference 99. <sup>i</sup> References 101, 102, 239, and 240. <sup>j</sup> Reference 216 (see also ref 215). <sup>k</sup> See also Figure 31.

31). Reber et al.<sup>217</sup> have observed a luminescence spectrum. Frum et al.<sup>218</sup> have observed a most interesting IR emission spectrum from a hot gas-phase fullerene sample. The frequencies of the observed bands are given in Table I.

The availability of significant quantities of fullerenes has also opened up a Round Postbuckminsterfullerene Era of polycyclic aromatic chemistry. Haufler et al.<sup>219</sup> found that  $\text{C}_{60}$  can undergo Birch reduction to produce a white solid of formula  $\text{C}_{60}\text{H}_{30}$ . They point out that this formula is consistent with a  $\text{C}_{60}$  hydrocarbon in

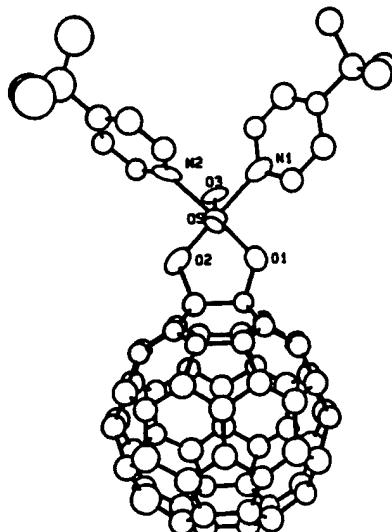
C<sub>60</sub> Buckminsterfullerene

Figure 32. ORTEP drawing (50% ellipsoids) of the one-to-one C<sub>60</sub>–osmium tetroxide adduct C<sub>60</sub>(OsO<sub>4</sub>)(4-tert-butylpyridine), showing the relationship of the osmium unit with the fullerene-60 carbon network.<sup>221</sup> (reprinted from ref 222; copyright 1991 the American Association for the Advancement of Science).

which 12 isolated double bonds remain, possibly in the pentagonal rings. The reduction appears to be reversible. Evidence for the existence of a C<sub>60</sub>U complex was obtained by the laser vaporization approach, used originally to detect C<sub>60</sub>La.<sup>7</sup> These authors also described the results of cyclic voltammetry measurements which indicated that C<sub>60</sub> has two reduction potentials. Similar measurements have been made by Allemand et al.<sup>220</sup> who obtained a third potential. Their cyclic voltammetry measurements indicate that, curiously, fullerenes-60 and -70 appear to exhibit similar electrochemical behavior.

In one of the first attempts to introduce functional groups, Hawkins et al.<sup>221</sup> have found that they can form adducts of fullerene-60 with OsO<sub>4</sub>(4-tert-butylpyridine) and its analogues. In a further study Hawkins et al.<sup>222</sup> have now obtained crystals of the osmium complex shown in Figure 32 and shown by X-ray analysis that rotation of the free C<sub>60</sub> spheroids in the solid phase has been eliminated by the attached group. This study has yielded the first carbon–carbon bond lengths for the fullerene cage (Table I). Arbogast et al.<sup>223</sup> have observed fascinating photophysical behavior: fullerene-60 shows no fluorescence and efficiently catalyzes the formation of singlet oxygen. These authors observe a small S–T splitting of ca. 9 kcal/mol which is probably due to the large diameter of the molecule and the resulting small electron–electron repulsion energy. This together with the very low fluorescence rate and probably large spin–orbit interaction appears to account for the fact that intersystem crossing is a dominant process. Attention has been drawn to the fact that, due to their photophysical activity, care should be taken when working with fullerenes.

Hare et al.<sup>224</sup> and Bethune et al.<sup>225</sup> have made infrared measurements on chromatographically separated sam-

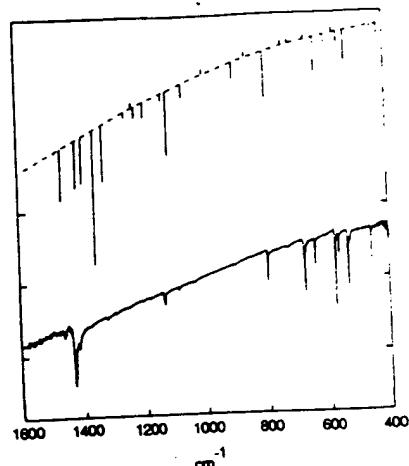


Figure 33. Infrared spectrum of chromatographically purified fullerene-70 obtained by Hare et al.<sup>224</sup> and compared with the calculated spectrum of Bakowies and Thiel.<sup>198,199</sup> The dashed curve is an estimated baseline. Note that the intensity of the very strong band calculated to lie near 1400 cm<sup>-1</sup> has been arbitrarily reduced by a factor of 3 relative to other features. Features calculated to be very weak are indicated by markers above the estimated baseline (reprinted from ref 224; copyright 1991 The Royal Society of Chemistry).

ene-70 together with the calculated spectrum of Bakowies and Thiel<sup>198,199</sup> is presented in Figure 33. Bethune et al.<sup>226</sup> and Dennis et al.<sup>227</sup> have also made Raman measurements of fullerene-60 and -70. Liquid-phase NMR studies of unpurified fullerene mixtures by Johnson et al.<sup>228</sup> confirmed the result of Taylor et al.<sup>6</sup> (carried out on fully chromatographically purified samples) that the fullerene-60 resonance is a single line. Ajie et al.<sup>215</sup> have also confirmed the NMR measurements of a single line for fullerene-60 and five lines for fullerene-70; the former on a separated sample, the latter on a mixed fullerene-60/-70 sample. A 2D NMR analysis on fullerene-70 by Johnson et al.<sup>229</sup> has unequivocally confirmed the assignments made previously by Taylor et al.<sup>6</sup> shown in Figures 29c and 30b. Further refinements by Fowler et al.<sup>214</sup> of previous studies<sup>210</sup> predict fullerene-60 chemical shifts in excellent agreement with experiment (within 3 ppm). The study also includes estimates of the shifts for fullerene-70 so supporting further the pattern of line assignments given by Taylor et al.<sup>6</sup> (Figures 29c and 30b). Tycko et al.<sup>230</sup> and Yannoni et al.<sup>231</sup> have made solid-state NMR measurements down to 177 K where the motion is sufficiently slow for chemical shift tensor data to be obtained. Fullerene-60 rotates isotropically at 296 K and fullerene-70 rotates somewhat more anisotropically. Haddon et al.<sup>232</sup> have measured the magnetic susceptibility of solid samples of fullerenes and found it consistent with a molecule with a small ring current (see discussion in section VIII). Fowler<sup>233</sup> notes that when this result is compared and contrasted with the NMR shift of fullerene-60<sup>6</sup> it may imply ambivalent character when the question of the molecules "aromaticity" is considered.

Perhaps scanning tunneling microscopy (STM) offers more than any other a satisfying feeling of what the

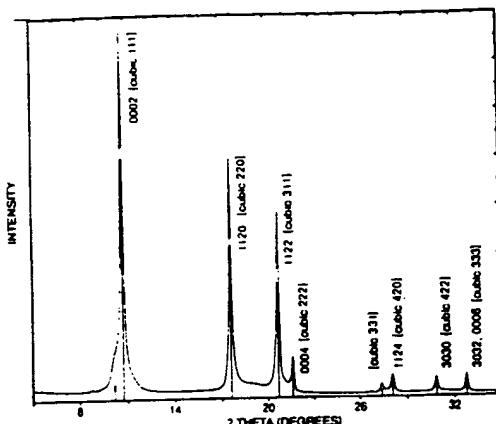


Figure 34. X-ray diffraction pattern obtained by MacKay et al.<sup>237</sup> from a chromatographically purified fullerene-60 sample. The structure revealed is basically that of a strongly disordered stacking of a simple hexagonal close-packing, exactly as for elemental cobalt. The hexagonal unit cell refines to  $a = 10.017 \pm 0.004 \text{ \AA}$  and  $c = 16.402 \pm 0.01$  and contains two  $C_{60}$  spheres. The spheres would be  $10.017 \text{ \AA}$  between centers and the calculated density would be  $1.68 \text{ g cm}^{-3}$ . The lines can be indexed as shown and it will be noted that, because of the stacking disorder, only those reciprocal lattice rows parallel to  $c$  for which  $-h + k = 3n$  are present. The  $c/a$  ratio of 1.637 is very close to the theoretical value of 1.633 and thus the pattern can also be indexed with respect to a face-centered cubic lattice (with  $a = 14.186 \text{ \AA}$ ) (as of copper metal) with stacking disorder which removes the 200 and 400 reflections and which introduces a very weak line (the first) at a spacing of  $a/(8/3)^{1/2}$  due to double diffraction from stacking faults. The intensity variation of the pattern as a whole corresponds to the transform of a sphere of radius  $3.5 \text{ \AA}$  giving a first minimum in the region of  $2\theta = 25^\circ$ . Since the crystal is a mixture of FCC and HCP arrays, extracted crystalline material probably contains solvent molecules trapped in the faults.

et al.<sup>235</sup> and Chen et al.<sup>236</sup> have deposited fullerene monolayers on gold and studied them by STM. The spherical molecules tend to form mobile hexagonally packed arrays on a surface. Chen et al.<sup>236</sup> observed local density variations on the surface of fullerene-60 which are highly suggestive of five- and six-membered rings.

The preliminary X-ray observations were made by Krätschmer et al.<sup>4</sup> working with crystalline material consisting mainly of fullerene-60 with some fullerene-70 present. A recent X-ray diffraction image was obtained by MacKay et al.<sup>237</sup> using chromatographically purified fullerene-60 (Figure 34). This image is commensurate with a completely random mix of HCP and FCC arrays of fullerene-60 molecules. Fleming et al.<sup>238</sup> obtained purely FCC structured crystals from vacuum sublimed material. The implication is that interstitially trapped solvent probably stabilizes the mixed FCC/HCP crystals. It appears that fullerene-60 spheres are rotating in the lattice<sup>231</sup> and that when rotation ceases at low temperature the crystals are still disordered at the atomic level.<sup>231,222,233</sup>

A most interesting study as far as theoretical chemistry is concerned is that of Lichtenberger et al.<sup>239,240</sup> who measured the photoelectron spectrum of fullerene-60 on a surface and in the gas phase (Figure 35). The results are in good agreement with the theoretical (DV)-X $\alpha$  study of Hale<sup>108</sup> (Figure 23). The first IP of fullerene-60, 7.61 eV, is nicely consistent with the result obtained by Zimmerman et al.<sup>101</sup> and McElvany.<sup>102</sup>

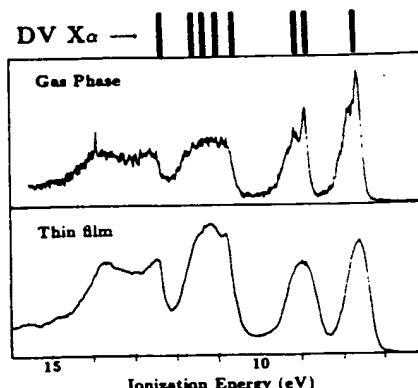


Figure 35. Gas phase (upper) and thin film (lower) He I valence photoelectron spectra of fullerene-60 obtained by Lichtenberger et al.<sup>239,240</sup> The DV-X $\alpha$  results of Hale<sup>108</sup> (see Figure 23) which appear to be in good agreement with observation are indicated (reprinted from ref 239; copyright 1991 Elsevier Science Publishers).

Luffer and Schram<sup>241</sup> have made electron ionization mass spectrometric measurements on fullerene-60.

Several papers presented at a special symposium on the fullerenes (Nov 1990) have been collected together and published by Averback et al.<sup>242</sup> Some of the most important experimentally determined properties of fullerenes are presented in the Table I.

## XI. Astrophysical Implications of $C_{60}$

Although low-temperature ion-molecule processes (Herbst and Klemperer<sup>243</sup> and Dalgarno and Black<sup>244</sup>) can account for most interstellar species, the long cyanopolyyne presented a problem. It was experiments which probed the possibility that carbon stars might be responsible for them<sup>21,22</sup> which revealed the stability of fullerene-60.<sup>3</sup> An important aspect of the experiments lay in the possibility of probing the conjecture of Douglas<sup>40</sup> that carbon chains might be responsible for the diffuse interstellar bands (DIBs). The DIBs are a set of interstellar optical absorption features of varying widths which have puzzled astronomers and spectroscopists since the mid-1930s. Herbig has published the definitive analysis of these features.<sup>245,246</sup> Many possible contenders for the carrier have been suggested, however no generally accepted explanation exists so far. This is strange as the species responsible is clearly abundant, chemically bound (i.e. not atomic), and must be quite stable in order to survive in the hostile interstellar environment or, if destroyed, be very efficiently reformed. The types of carrier appear to be few in number and must have very large electronic absorption coefficients.

The possibility that  $C_{60}$  might be the widely distributed in the Universe and particularly in the outflows from carbon stars was suggested when the original discovery of its stability was made.<sup>3</sup> It was also pointed out that the fullerene-60 surface might be an important site for the catalysis of interstellar reactions and perhaps it (or a derivative) might be responsible for such features as the DIBs. There is one key argument, associated with the proposal that fullerene analogues (ionized or un-ionized, complexed or otherwise) may be

the carriers has that all previous suggestions do not: fullerene-60 and its analogues are unique in that they appear to survive the violent processes which occur when the atomic components of a chaotic plasma condense to form particles. Various aspects of this original conjecture, particularly with regard to possible derivatives such as intracage complexes both ionized and neutral, have been discussed<sup>55-58</sup> in general terms.

As far as the neutral fullerene-60 species in space is concerned, the negative results of searches based on the laboratory measurement<sup>28</sup> has been published by Snow and Seab<sup>247</sup> and Sommerville and Bellis.<sup>248</sup>

The conditions in the ISM are such that a large fraction of any fullerene-60 molecules present is likely to be ionized and thus it has been pointed out that the spectra of ionized fullerenes such as C<sub>60</sub><sup>+</sup> or fullerene analogues (such as the cage complexes C<sub>60</sub>M<sup>+</sup>) might be responsible for some astrophysical features.<sup>55,57</sup> Léger et al.<sup>249</sup> and Joblin et al.<sup>250</sup> have taken up the C<sub>60</sub><sup>+</sup> proposal and considered it further.

Complexed species (section VIII) in the interstellar medium are particularly interesting as any C<sub>60</sub> present is likely to be ionized and probably have something stuck to its surface. As the DIBs exhibit features reminiscent of matrix spectra, the possibility that intracage complexes<sup>55,57,201-203</sup> as well as the extracage complexes<sup>202</sup> might be responsible has been discussed. Heymann<sup>200</sup> has considered the He intracage complexes and Ballester et al. other likely species containing O, Na, etc.<sup>201</sup> Kroto and Jura<sup>202</sup> draw particular attention to the fact that the charge transfer bands of the (C<sub>60</sub>M)<sup>+</sup> intracage complex and the van der Waals extracage complex (C<sub>60</sub>)<sup>+</sup>·M (M = alkali, alkaline earth, or other element) are likely to be very strong. Particularly interesting are possible relationships that charge-transfer transitions might have with the DIBs and perhaps also the strong unassigned 2170 Å absorption feature which has puzzled astronomers for over seven decades. Hoyle and Wickramasinghe<sup>251</sup> suggested that C<sub>60</sub> itself might explain this feature and further calculations relating to this possibility have been discussed by Braga et al.<sup>167</sup> Rabilizirov<sup>252</sup> has also discussed these possibilities. Wright<sup>253</sup> has discussed the general optical/UV characteristics of fullerenes and concludes that the observed interstellar extinction is not consistent with the presence of significant quantities of spheroidal particles with graphite-like outer shells. In this respect the existence of the amorphous carbon surface layers surrounding the graphite cores of carbon microparticles may well be important.<sup>116</sup> From the UV/vis spectra obtained so far<sup>215,216</sup> it is clear that neutral fullerene-60 is not responsible for either the DIBs or the 2170 Å hump.

There are also some intriguing interstellar emission features in the IR, termed the unidentified infrared bands (UIBs), which have been assigned to PAH-like material by Duley and Williams,<sup>254</sup> Léger and Puget,<sup>255</sup> and Allamandola et al.<sup>256</sup> The assignment rests largely on the reasonable correspondence between the astrophysical frequencies and those of polycyclic aromatic molecules which are usually used for fingerprint identification of large PAHs. Balm and Kroto<sup>257</sup> have discussed the fact that, if the fullerene-60 concept is correct, PAH material in space is likely to be nonplanar. They point out that one feature, namely that at 11.3

The new results also offer possible new avenues of study as far as condensed carbonaceous matter in the cosmos is concerned. According to McKay et al.<sup>258</sup> caged carbon clusters may offer a plausible explanation of some of the isotope anomalies observed in the elemental analysis of carbonaceous chondrites particularly the <sup>22</sup>Ne anomaly. Clayton<sup>259</sup> has pointed out that condensation in the atmospheres of supernovae might explain the so-called Ne-E anomaly. McKay et al.<sup>258</sup> have suggested that this observation might be explained by encapsulation of <sup>22</sup>Na in fullerene cages or icosiprismatic embryos during the dust formation phases that follow supernova and nova outbursts. Subsequently, the decay of <sup>22</sup>Na yields an encapsulated <sup>22</sup>Ne atom. Zinner et al.<sup>260</sup> have pointed out that isotope anomalies are only to be found in spheroidal carbon grains. So far the only evidence that C<sub>60</sub> might exist in space is an unconfirmed report by Anderson.<sup>261</sup>

## XII. Conclusions

It took some 15 or so years before the imaginative theoretical conjectures of Osawa and Yoshida<sup>13,14</sup> and Bochvar and Gal'pern<sup>17,18</sup> were realized in the discovery of the stability of the C<sub>60</sub> mass spectrometric signal<sup>3</sup> in 1985. A further period of five years elapsed during which time many experimental measurements and theoretical studies were made. By-and-large the theoretical work (section VIII) substantiated the idea that buckminsterfullerene should be stable. As time elapsed the weight of circumstantial evidence grew and ultimately became convincing. The key observations include:

- (1) Detection of monometallic complexes indicated that atom encapsulation was feasible.<sup>7,96</sup>
- (2) Further cluster beam studies showed 60 to be a magic number whether the carbon species was positively or negatively charged or neutral.<sup>54,56,52</sup>
- (3) Reactivity studies showed the molecule to possess an inertness that was consistent with closure and the absence of dangling bonds.<sup>103,96</sup>
- (4) The pentagon isolation principle explained the observation of C<sub>60</sub> as the first magic number and C<sub>70</sub> as the second.<sup>8,9</sup> Thus it was shown that the fullerene hypothesis rested on the observation of two magic numbers and not just one. Further refinement of the geodesic principle explained other observed magic numbers.<sup>49</sup>
- (5) Large fullerene networks were found to possess quasiicosahedral structures and thus related giant concentric cage species<sup>108</sup> appeared to explain the infrastructure of the carbon microparticles observed by Iijima.<sup>109,110</sup>
- (6) Photoelectron measurements of Yang et al.<sup>99</sup> were also quite consistent with the fullerene conjecture.

These and other studies (discussed in sections V-VII) thus had laid the background against which the critical infrared observation of Krätschmer et al.<sup>5,74</sup> was made. They were led to make this observation by considering that some intriguing optical features observed in 1982 might be due to buckminsterfullerene. These observations were followed up by Krätschmer, Lamb, Fostiropoulos, and Huffman<sup>4</sup> and Taylor et al.,<sup>6</sup> and the results have revolutionized the field in that now the material can be made in quantity and the properties of

It is interesting to note that the motives for the experiments which serendipitously revealed the spontaneous creation and remarkable stability<sup>3</sup> of C<sub>60</sub> were astrophysical. Behind this goal lay a quest for an understanding of the curiously pivotal role that carbon plays in the origin of stars, planets, and biospheres. Behind the recent breakthrough of Krätschmer et al. in producing macroscopic amounts of fullerene-60, lay similar astrophysical ideas.<sup>4</sup> It is fascinating to now ponder over whether buckminsterfullerene is distributed throughout space, and we have not recognized it, and that it may have been under our noses on earth, or at least played an important role in some very common environmental processes, since time immemorial.

The material is already exhibiting novel physical and chemical properties and there can be little doubt that an exciting field of chemistry and materials science, with many exciting applications has opened up. One of its most important properties is its ability to accept electrons. The low-lying LUMO causes it to be a soft electrophile.

It is perhaps worthwhile noting that C<sub>60</sub> might have been detected in a sooty flame decades ago and that our present enlightenment has been long delayed. How serious this delay has been only time will tell; however, already fullerene chemistry is a vibrant field of study and the prospects for new materials with novel properties is most promising. Certainly, a New Round Postbuckminsterfullerene World of carbon chemistry appears to have been discovered, almost overnight. It should not be long before the molecule becomes a standard in textbooks; indeed construction procedures for fullerene-60 and giant fullerenes are to be found in the educational literature.<sup>126,262</sup>

### Warning

The UCLA group has pointed out the importance of treating the material with great caution at this time when so little is known about it.<sup>263</sup> Its ability to catalyze the formation of singlet oxygen and its novel chemical behavior inevitably suggest the possibility that the fullerenes might be carcinogenic. Particular care should be taken to ensure that the dust is not inhaled during preparation of the soot itself.

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### References

- Palmer, H.; Shelef, M. *Chemistry and Physics of Carbon*; Walker, J. R., Jr., Ed.; Marcel Dekker: New York, 1967; Vol. 4, pp 85-135.
- Weitner, W., Jr.; Van Zee, R. J. *Chem. Rev.* 1989, 89, 1713-1747.
- Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature (London)* 1985, 318, 162-163.
- Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature (London)* 1990, 347, 354-358.
- Krätschmer, W.; Fostiropoulos, K.; Huffman, D. R. *Dusty Objects in the Universe*; Bussolati, E., Vittone, A. A., Eds.; Kluwer: Dordrecht, 1990 (Conference in 1989).
- Taylor, R.; Hare, J. P.; Abdul-Sada, A. K.; Kroto, H. W. *J. Chem. Soc., Chem. Commun.* 1990, 1423-1425.
- Heath, J. R.; O'Brien, S. C.; Zhang, Q.; Liu, Y.; Curl, R. F.; Kroto, H. W.; Smalley, R. E. *J. Am. Chem. Soc.* 1985, 107, 7779-7780.
- Kroto, H. W. *Nature (London)* 1987, 329, 529-531.
- Schmalz, T. G.; Seitz, W. A.; Klein, D. J.; Hite, G. E. *J. Am. Chem. Soc.* 1988, 110, 1113-1127.
- Kroto, H. W.; Walton, D. R. M. *Chemistry of Three Dimensional Polycyclic Molecules*; Osawa, E., Yonemitsu, O., Eds.; Verlag Chemie International: Weinheim, in press.
- Lawlor, R. *Sacred Geometry*; Crossroad: New York, 1974.
- Reti, L., Ed. *The Unknown Leonardo*; McGraw Hill: New York, 1974; pp 71.
- Osawa, E. *Kagaku (Kyoto)* 1970, 25, 854-863 (in Japanese); *Chem. Abstr.* 1971, 74, 75698v.
- Yoshida, Z.; Osawa, E. *Aromaticity*; Kagaku-dojin: Kyoto, 1971; pp 174-178 (in Japanese).
- Jones, D. E. *New Sci.* 32 (3 Nov) 1966, 245.
- Jones, D. E. H. *The Inventions of Daedalus*; Freeman: Oxford, 1982; pp 118-119.
- Bochvar, D. A.; Gal'pern, E. G. *Dokl. Akad. Nauk SSSR* 1973, 209, 610-612; *Proc. Acad. Sci. USSR* 1973, 209, 239-241 (English translation).
- Stankevich, I. V.; Nikerov, M. V.; Bochvar, D. A. *Russ. Chem. Rev.* 1984, 53(7), 640-655.
- Davidson, R. A. *Theor. Chim. Acta* 1981, 58, 193-195.
- Haymet, A. D. J. *Chem. Phys. Lett.* 1985, 122, 421-424.
- Dörnenburg, E.; Hintenberger, H. *Z. Naturforsch. Teil A* 1959, 14A, 765-767.
- Dörnenburg, E.; Hintenberger, H.; Franzen, J. *Z. Naturforsch. Teil A* 1961, 16A, 532-534.
- Franzen, J.; Hintenberger, H. *Z. Naturforsch. Teil A* 1961, 16A, 535-539.
- Hintenberger, H.; Franzen, J.; Schuy, K. D. Z. *Naturforsch. Teil A* 1963, 18A, 1236-1237.
- Robling, E. A.; Cox, D. M.; Kaldor, A. *J. Chem. Phys.* 1984, 81, 3322-3330.
- Dietz, T. G.; Duncan, M. A.; Powers, D. E.; Smalley, R. E. *J. Chem. Phys.* 1981, 74, 6511-6512.
- Kaldor, A.; Cox, D. M.; Trevor, D. J.; Whetten, R. L. *Catalysis Characterisation Science*; Deviney, M. L.; Gland, J. L., Eds.; American Chemical Society: Washington, DC, 1985; pp 111-123.
- Bloomfield, L. A.; Geusic, M. E.; Freeman, R. R.; Brown, W. L. *Chem. Phys. Lett.* 1985, 121, 33-37.
- Heath, J. R.; Zhang, Q.; O'Brien, S. C.; Curl, R. F.; Kroto, H. W.; Smalley, R. E. *J. Am. Chem. Soc.* 1987, 109, 359-363.
- Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Astrophys. J.* 1987, 314, 352-355.
- Kroto, H. W. *Chem. Soc. Rev.* 1982, 11, 435-491.
- Kroto, H. W. *Int. Rev. Phys. Chem.* 1981, 1, 309-376.
- Alexander, A. J.; Kroto, H. W.; Walton, D. R. M. *J. Mol. Spec.* 1976, 62, 175-180.
- Kirby, C.; Kroto, H. W.; Walton, D. R. M. *J. Mol. Spec.* 1980, 261-265.
- Oka, T. *J. Mol. Spec.* 1978, 72, 172-174.
- Avery, L. W.; Broten, N. W.; Macleod, J. M.; Oka, T.; Kroto, H. W. *Astrophys. J.* 1976, 205, L173-L175.
- Kroto, H. W.; Kirby, C.; Walton, D. R. M.; Avery, L. W.; Broten, N. W.; Macleod, J. M.; Oka, T. *Astrophys. J.* 1978, 219, L133-L137.
- Broten, N. W.; Oka, T.; Avery, L. W.; Macleod, J. M.; Kroto, H. W. *Astrophys. J.* 1978, 223, L105-L107.
- Bell, M. B.; Feldman, P. A.; Kwok, S.; Matthews, H. E. *Nature (London)* 1982, 295, 389-391.
- Douglas, A. E. *Nature (London)* 1977, 269, 130-132.
- Michalopoulos, D. L.; Geusic, M. E.; Langridge-Smith, P. R.; Smalley, R. E. *J. Chem. Phys.* 1984, 80, 3556-3560.
- Kroto, H. W. *Proc. R. Inst.* 1986, 58, 45-72.
- Fuller, R. B. *Inventions—The Patented Works of Buckminster Fuller*; St. Martin's Press: New York, 1983.
- Nickon, A.; Silversmith, E. F. *Organic Chemistry—The Name Game: Modern Coined Terms and Their Origins*; Pergamon: New York, 1987; pp 214-215.
- Stewart, P. J. *Nature (London)* 1986, 319, 444.
- Kroto, H. W. *Nature (London)* 1986, 322, 766.
- Rose, P. Private communication (Figure 7).
- Castella, J.; Serratos, F. *J. Chem. Ed.* 1988, 60, 941.
- Castella, J.; Serratos, F. *J. Chem. Ed.* 1988, 63, 630.
- Kroto, H. W. *Science* 1988, 242, 1139-1145.
- Curl, R. F.; Smalley, R. E. *Science* 1988, 242, 1017-1022.
- Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Kroto, H. W.; Smalley, R. E. *Comments Condens. Matter Phys.* 1987, 13, 119-141.
- Smalley, R. E. *Carbon in the Galaxy*; Tarter, J. C., Chang, S., DeFreeze, D. J., Eds.; National Aeronautics and Space Administration Conference Publication 3061: Washington, DC, 1990; pp 199-244.

(54) Smalley, R. E. *Atomic and Molecular Clusters*; Bernstein, E. R., Ed.; Elsevier: Amsterdam, 1990; pp 1-68.

(55) Kroto, H. W. *Polyyclic Aromatic Hydrocarbons and Astrophysics*; Leger, A., d'Hendecourt, L. B., Eds.; Reidel: Dordrecht, 1987; pp 197-206.

(56) Kroto, H. W. *Phil. Trans. R. Soc. Lond. A* 1988, **325**, 405-421.

(57) Kroto, H. W. *Ann. Phys. Fr.* 1989, **14**, 169-179.

(58) Kroto, H. W. *Carbon in the Galaxy*; Tarter, J. C., Chang, S., DeFrees, D. J., Eds.; National Aeronautics and Space Administration Conference Publication 8061: Washington, DC, 1990; pp 275-284.

(59) Kroto, H. W. *Math. Appl.* 1989, **17**, 417-423.

(60) Kroto, H. W. *Chem. Brit.* 1990, **26**, 40-45.

(61) Kroto, H. W. *Pure Appl. Chem.* 1990, **62**, 407-415.

(62) Hirota, E. *Kagaku (Kyoto)* 1986, **41**, 534-535 (in Japanese); *Chem. Abstr.* 1987, **107**, 107957x.

(63) Heath, J. R. *Spectroscopy* 1990, **5**, 36-43.

(64) Liu, Y.; O'Brien, S. C.; Zhang, Q.; Heath, J. R.; Tittel, F. K.; Curl, R. F.; Kroto, H. W.; Smalley, R. E. *Chem. Phys. Lett.* 1986, **126**, 215-217.

(65) Hahn, M. Y.; Hones, E. C.; Paguia, A. J.; Schriver, K. E.; Camarena, A. M.; Whetten, R. L. *Chem. Phys. Lett.* 1986, **130**, 12-16.

(66) O'Brien, S. C.; Heath, J. R.; Kroto, H. W.; Curl, R. F.; Smalley, R. E. *Chem. Phys. Lett.* 1986, **132**, 99-102.

(67) Cox, D. M.; Reichmann, K. C.; Kaldor, A. J. *Chem. Phys.* 1988, **88**, 1588-1597.

(68) O'Keefe, A.; Ross, M. M.; Baronavski, A. P. *Chem. Phys. Lett.* 1986, **130**, 17-19.

(69) Pradel, P.; Monchicourt, P.; Laucagne, J. J.; Perdrix, M.; Watel, G. *Chem. Phys. Lett.* 1989, **158**, 412-416.

(70) McElvany, S. W.; Nelson, H. H.; Baronavski, A. P.; Watson, C. H.; Eyler, J. R. *Chem. Phys. Lett.* 1987, **134**, 214-219.

(71) McElvany, S. W.; Dunlap, B. I.; O'Keefe, J. J. *Chem. Phys.* 1987, **86**, 715-725.

(72) Meijer, G.; Bethune, D. S. *Chem. Phys. Lett.* 1990, **175**, 1-2.

(73) Meijer, G.; Bethune, D. S. *J. Chem. Phys.* 1990, **93**, 7800-7802.

(74) Krätschmer, W.; Fostiropoulos, K.; Huffman, D. R. *Chem. Phys. Lett.* 1990, **170**, 167-170.

(75) Creasy, W. R.; Brenna, J. T. *J. Chem. Phys.* 1990, **92**, 2269-2279.

(76) Creasy, W. R.; Brenna, J. T. *Chem. Phys.* 1988, **126**, 453-468.

(77) Campbell, E. E. B.; Ulmer, G.; Hasselberger, B.; Busmann, H.-G.; Hertel, I. V. *J. Chem. Phys.* 1990, **93**, 6900-6907.

(78) Hasselberger, B.; Busmann, H.-G.; Campbell, E. E. B. *Appl. Surf. Sci.* 1990, **46**, 272-278.

(79) Campbell, E. E. B.; Ulmer, G.; Busmann, H.-G.; Hertel, I. V. *Chem. Phys. Lett.* 1990, **175**, 505-510.

(80) Greenwood, P. F.; Strachan, M. G.; El-Nakat, H. J.; Willett, G. D.; Wilson, M. A.; Attalla, M. I. *Fuel* 1990, **69**, 257-260.

(81) Giardini Guidoni, A.; Teghil, R.; Morone, A.; Sica, M.; Mele, A.; Letardi, T.; Di Lazzaro, P. *Proceedings of Laser 89 Conference*, manuscript 0913, in press.

(82) Lineman, D. N.; Samayajula, K. V.; Sharkey, A. G.; Hercules, D. M. *J. Phys. Chem.* 1989, **93**, 5025-5026.

(83) Lineman, D. N.; Viswanadham, S. K.; Sharkey, A. G.; Hercules, D. M. *Microbeam Anal.* 1989, **24**, 297-298.

(84) So, H. Y.; Wilkins, C. L. *J. Phys. Chem.* 1989, **93**, 1184-1187.

(85) Rubin, Y.; Kahr, M.; Knobler, C. B.; Diederich, F.; Wilkins, C. L. *J. Am. Chem. Soc.* 1991, **113**, 495-500.

(86) Diederich, F.; Rubin, Y.; Knobler, C. B.; Whetten, R. L.; Schriver, K. E.; Houk, K. N.; Li, Y. *Science* 1989, **245**, 1088-1090.

(87) Gerhardt, Ph.; Löffler, S.; Homann, K. *Chem. Phys. Lett.* 1987, **137**, 306-310.

(88) Gerhardt, Ph.; Homann, K. H.; Löffler, S.; Wolf, H. *AGARD Conf. Proc.* 1987, **422**, 22-(1-11).

(89) Gerhardt, Ph.; Löffler, S.; Homann, K. H. *Symposium on Combustion* 1988, **22**, 395-401.

(90) Gerhardt, Ph.; Homann, K. H. *J. Phys. Chem.* 1990, **94**, 5381-5391.

(91) Cox, D. M.; Trevor, D. J.; Reichmann, K. C.; Kaldor, A. J. *Am. Chem. Soc.* 1986, **108**, 2457-2458.

(92) Radi, P. P.; Bunn, T. L.; Kemper, P. R.; Molchan, M. E.; Bowers, M. T. *J. Chem. Phys.* 1988, **88**, 2809-2814.

(93) Radi, P. P.; Hsu, M. T.; Brodbelt-Lutzig, J.; Rincon, M. E.; Bowers, M. T. *J. Chem. Phys.* 1990, **92**, 4817-4822.

(94) Radi, P. P.; Hsu, M. T.; Rincon, M. E.; Kemper, P. R.; Bowers, M. T. *Chem. Phys. Lett.* 1990, **174**, 223-229.

(95) O'Brien, S. C.; Heath, J. R.; Curl, R. F.; Smalley, R. E. *J. Chem. Phys.* 1988, **88**, 220-230.

(96) Weiss, F. D.; Elkind, J. L.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *J. Am. Chem. Soc.* 1988, **110**, 4464-4465.

(97) Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Kroto, H. W.; Smalley, R. E. Unpublished observations.

(98) Heath, J. R.; Curl, R. F.; Smalley, R. E. *J. Chem. Phys.* 1987, **87**, 4236-4238.

(99) V... C. U. Battista, C. I.; Conneran, J.; Cheshnovsky, O.;

(100) Cheshnovsky, O.; Yang, S. H.; Pettiette, C. L.; Craycraft, M. J.; Liu, Y.; Smalley, R. E. *Chem. Phys. Lett.* 1987, **138**, 119-124.

(101) Zimmerman, J. A.; Eyler, J. R.; Bach, S. B. H.; McElvany, S. W. *J. Chem. Phys.* 1991, **94**, 3556-3562.

(102) McElvany, S. W. *Int. J. Mass Spectrom. Ion Process.* 1990, **102**, 81-98.

(103) Zhang, Q. L.; O'Brien, S. C.; Heath, J. R.; Liu, Y.; Curl, R. F.; Kroto, H. W.; Smalley, R. E. *J. Phys. Chem.* 1986, **90**, 525-528.

(104) Kohlring, E. A. *J. Chem. Phys.* 1990, **93**, 7851-7862.

(105) Hallett, R. A.; McKay, K. G.; Balm, S. P.; Allaf, A. W.; Kroto, H. W.; Stace, A. J. In press.

(106) Doverstol, M.; Lindgren, B.; Sassenberg, U.; Yu, H. *Phys. Scripta* 1991, in press.

(107) Fowler, P. W.; Steer, J. I. *J. Chem. Soc., Chem. Commun.* 1987, **1403**-1405.

(108) Kroto, H. W.; McKay, K. G. *Nature (London)* 1988, **331**, 328-331.

(109) Iijima, S. *J. Cryst. Growth* 1989, **5**, 675-683.

(110) Iijima, S. *J. Phys. Chem.* 1987, **91**, 3466-3467.

(111) McKay, K. G.; Wales, D. J.; Kroto, H. W. To be published.

(112) Kroto, H. W. *J. Chem. Soc., Faraday Trans.* 1990, **86**, 2465-2468.

(113) Roush, S. A.; Dunne, L. J.; Clark, A. D.; Chaplin, M. F. *Philos. Mag.* 1990, **62**, 243-260.

(114) Yacaman, M. J.; Cox, D.; Chianelli, R.; Kaldor, A. *Icosahedral Spirals in Giant Fullerenes Solids*. In preparation.

(115) Yacaman, M. J. *Proceedings of Symposium G on Clusters and Cluster-Assembled Materials*, Mater. Res. Soc. Proc., Averbeck, R. S.; Nelson, D. L.; Bernholc, J., Eds.; MRS Publications: New York, 1991.

(116) Kroto, H. W.; Iijima, S. In press.

(117) Wales, D. J. *Chem. Phys. Lett.* 1987, **141**, 478-484.

(118) Bernholc, J.; Phillips, J. C. *J. Chem. Phys.* 1986, **85**, 3258-3267.

(119) Kroto, H. W. *19th Biennial Conference on Carbon*; American Carbon Society, 1989; pp 394-395.

(120) Frenklach, M.; Ebert, L. B. *J. Phys. Chem.* 1988, **92**, 561-563.

(121) Ebert, L. B.; Scanlon, J. C.; Clausen, C. A. *Energy Fuels* 1988, **2**, 438-445.

(122) Ebert, L. B.; Kastrup, R. V.; Scanlon, J. C.; Sherwood, R. D. *19th Biennial Conference on Carbon*, American Carbon Society, 1989; pp 396-397.

(123) Ebert, L. B. *Science* 1990, **247**, 1468-1471.

(124) Harris, S. J.; Weiner, A. M. *Ann. Rev. Phys. Chem.* 1985, **36**, 31-52.

(125) Kroto, H. W. To be published.

(126) Kroto, H. W.; McKay, K. G. *J. Chem. Ed.* To be submitted.

(127) Stone, A. J.; Wales, D. J. *Chem. Phys. Lett.* 1986, **128**, 501-503.

(128) Takai, T.; Lee, C.; Halicioglu, T.; Tiller, W. A. *J. Phys. Chem.* 1990, **94**, 4480-4482.

(129) Balm, S. P.; Allaf, A. W.; Kroto, H. W.; Murrell, J. N. *J. Chem. Soc., Faraday Trans.* 1991, **87**, 803-806.

(130) Zerbetto, F. *Chem. Phys. Lett.* 1991, **150**, 39-45.

(131) Ballico, F.; Milani, P. *Phys. Rev. B* 1990, **42**, 3201-3204.

(132) Schmalz, T. G.; Seitz, W. A.; Klein, D. J.; Hite, G. E. *Chem. Phys. Lett.* 1986, **130**, 203-207.

(133) Hosoya, H. *Comp. Maths. Appl.* 1986, **12**, 271-275.

(134) Brendsdal, E.; Cyvin, S. J. *THEOCHEM* 1989, **57**, 55-66.

(135) Eber, V. *Counting the Kekulé Structures of Buckminsterfullerene*. Personal communication.

(136) Klein, D. J.; Schmalz, T. G.; Hite, G. E.; Seitz, W. A. *J. Am. Chem. Soc.* 1986, **108**, 1301-1302.

(137) Klein, D. J.; Seitz, W. A.; Schmalz, T. G. *Nature (London)* 1986, **323**, 703-706.

(138) Randic, M.; Nicolic, S.; Trinajstic, N. *Croat. Chem. Acta* 1987, **60**, 595-604.

(139) Nicolic, S.; Trinajstic, N. *Kem. Ind. (Zagreb)* 1987, **36**, 107-111.

(140) Amic, D.; Trinajstic, N. *J. Chem. Soc., Perkin Trans. 2* 1990, 1595-1598.

(141) Balasubramanian, K.; Liu, X. *J. Comput. Chem.* 1988, **9**, 406-415.

(142) Balasubramanian, K. *Chem. Phys. Lett.* 1990, **175**, 273-278.

(143) Diaa, J. R. *J. Chem. Educ.* 1989, **66**, 1012-1015.

(144) Haymet, A. D. J. *J. Am. Chem. Soc.* 1986, **108**, 319-321.

(145) Jiang, Y.; Zhang, H. *Theor. Chem. Acta* 1989, **75**, 279-297.

(146) Hess, B. A.; Shaad, L. J. *J. Org. Chem.* 1986, **51**, 3902-3903.

(147) Aihara, J.; Hosoya, H. *Bull. Chem. Soc. Jpn.* 1988, **61**, 2657-2659.

(148) Fowler, P. W.; Woolrich, J. *Chem. Phys. Lett.* 1986, **127**, 78-83.

(149) Fowler, P. W. *Chem. Phys. Lett.* 1986, **131**, 444-450.

(150) Fowler, P. W.; Cremona, J. E.; Steer, J. L. *Theor. Chem. Acta* 1988, **73**, 1-26.

(151) Fowler, P. W. *J. Chem. Soc., Faraday Trans.* 1990, **86**,

(152) Ceulemans, A.; Fowler, P. W. *Phys. Rev. A* 1989, 39, 481-493.

(153) Ceulemans, A.; Fowler, P. W. *J. Chem. Phys.* 1990, 93, 1221-1234.

(154) Byers Brown, W. *Chem. Phys. Lett.* 1987, 136, 128-133.

(155) Coulombeau, C.; Rassat, A. J. *J. Chim. Phys. Phys.-Chim. Biol.* 1987, 84, 875-882.

(156) Ozaki, M.; Takahashi, A. *Chem. Phys. Lett.* 1986, 127, 242-244.

(157) Haddon, R. C.; Brus, L. E.; Raghavachari, K. *Chem. Phys. Lett.* 1986, 125, 459-464.

(158) Haddon, R. C.; Brus, L. E.; Raghavachari, K. *Chem. Phys. Lett.* 1986, 131, 165-169.

(159) Bochar, D. A.; Gal'pern, E. G.; Stankevich, I. V. *Zh. Strukt. Khim.* 1989, 30, 38-43 (in Russian).

(160) Feng, J.; Li, J.; Wang, Z.; Zerner, M. C. *Int. J. Quantum Chem.* 1990, 37, 599-607.

(161) Newton, M. D.; Stanton, R. E. *J. Am. Chem. Soc.* 1986, 108, 2469-2470.

(162) McKee, M. L.; Herndon, W. C. *J. Mol. Struct.* 1987, 153, 75-84.

(163) Lüthi, H. P.; Almköf, J. *J. Chem. Phys. Lett.* 1987, 135, 357-360.

(164) Almköf, J.; Lüthi, H. P. *ACS Symp. Ser.* 1987, 353 (Supercomput. Res. Chem. Chem. Eng.), 35-48.

(165) Almköf, J. *Carbon in the Galaxy*; Tarter, J. C., Chang, S., DeFreez, D. J., Eds.; National Aeronautics and Space Administration Conference Publication 3061: Washington, DC, 1990; pp 245-258.

(166) Larsson, S.; Volosov, A.; Rosen, A. *Chem. Phys. Lett.* 1987, 137, 501-504.

(167) Braga, M.; Larsson, S.; Rosen, A.; Volosov, A. *Astron. Astrophys.* 1991, 245, 223-238.

(168) Schulman, J. M.; Disch, R. L. *J. Chem. Soc., Chem. Comm.* 1991, 411-412.

(169) Hale, P. D. *J. Am. Chem. Soc.* 1986, 108, 6087-6088.

(170) Satpathy, S. *Chem. Phys. Lett.* 1986, 130, 545-550.

(171) Marynick, D. S.; Estreicher, S. *Chem. Phys. Lett.* 1986, 132, 383-386.

(172) Kovacević, K.; Graovac, A.; Babić, D. *Int. J. Quantum Chem. Symp.* 1987, 21, 589-593.

(173) Haddon, R. C. *J. Am. Chem. Soc.* 1990, 112, 3385-3389.

(174) Fabre, C.; Rassat, A. *C.R. Acad. Sci. Paris* 1990, t. 308 II, 1223-1228.

(175) Kataoka, M.; Nakajima, T. *Tetrahedron* 1986, 42, 6437-6442.

(176) Lefádo, I.; Udvardi, L. *Chem. Phys. Lett.* 1987, 136, 418-422.

(177) Shibuya, T.-I.; Yohitani, M. *Chem. Phys. Lett.* 1987, 137, 13-16.

(178) Hayden, G. W.; Mele, E. *J. Phys. Rev. B* 1987, 36, 5010-5015.

(179) Negri, F.; Orlando, G.; Zerbetto, F. *Chem. Phys. Lett.* 1988, 144, 31-37.

(180) Wu, Z. C.; Jelaki, D. A.; George, T. F. *Chem. Phys. Lett.* 1987, 137, 291-294.

(181) Disch, R. L.; Schulman, J. M. *Chem. Phys. Lett.* 1986, 125, 465-466.

(182) Schulman, J. M.; Disch, R. L.; Miller, M. A.; Peck, R. C. *Chem. Phys. Lett.* 1987, 141, 45-47.

(183) Coulombeau, C.; Rassat, A. J. *J. Chim. Phys. Phys.-Chim. Biol.* 1987, 84, 875-882.

(184) Coulombeau, C.; Rassat, A. J. *J. Chim. Phys. Phys.-Chim. Biol.* 1988, 85, 369-374.

(185) Weeks, D. E.; Harter, W. G. *Chem. Phys. Lett.* 1986, 132, 387-392.

(186) Weeks, D. E.; Harter, W. G. *Chem. Phys. Lett.* 1988, 144, 366-372.

(187) Weeks, D. E.; Harter, W. G. *J. Chem. Phys.* 1989, 90, 4727-4743.

(188) Weeks, D. E.; Harter, W. G. *J. Chem. Phys.* 1989, 90, 4744-4771.

(189) Weeks, D. E.; Harter, W. G. *Chem. Phys. Lett.* 1991, 176, 209-216.

(190) Stanton, R. E.; Newton, M. D. *J. Phys. Chem.* 1988, 92, 2141-2145.

(191) Cyvin, S. J.; Brendsdal, E.; Cyvin, B. N.; Brunvoll, J. *Chem. Phys. Lett.* 1988, 143, 377-380.

(192) Brendsdal, E.; Cyvin, B. N.; Brunvoll, J.; Cyvin, S. J. *Spectrosc. Lett.* 1988, 21, 313-318.

(193) Brendsdal, E. *Spectrosc. Lett.* 1988, 21, 319-339.

(194) Slanina, Z.; Rudzinski, J. M.; Togasi, M.; Osawa, E. *THEOCHEM* 1989, 61, 169-176.

(195) Slanina, Z.; Rudzinski, J. M.; Osawa, E. *Collect. Czech. Chem. Commun.* 1987, 52, 2831-2838.

(196) Slanina, Z.; Rudzinski, J. M.; Osawa, E. *Carbon* 1987, 25, 747-750.

(197) Rudzinski, J. M.; Slanina, Z.; Togasi, M.; Osawa, E.; Iizuka, T. *Thermochim. Acta* 1988, 125, 155-162.

(198) Bakowies, D.; Thiel, W. J. *Am. Chem. Soc.* 1991, 113, 3704-3714.

(199) Bakowies, D.; Thiel, W. J. *Chem. Phys.* 1991, 151, 309-321.

(200) Heymann, D. J. *Geophys. Res. B* 1986, 91, B135-138.

(201) Ballester, J. L.; Antoniewicz, P. R.; Smoluchowski, R. *Astro-*

(202) Krato, H. W.; Jura, M. In press.

(203) Rosen, A.; Waastberg, B. *J. Am. Chem. Soc.* 1988, 110, 8701-8703.

(204) Rosen, A.; Waastberg, B. *Z. Phys. D: At. Mol. Clusters* 1989, 12, 387-390.

(205) Saito, S. *Proceedings of Symposium G on Clusters and Cluster-Assembled Materials. Mater. Res. Soc. Proc.*; Averback, R. S.; Nelson, D. L.; Bernholc, J., Eds.; MRS Publications: New York, 1991.

(206) Scuseria, G. E. *Chem. Phys. Lett.* 1991, 176, 423-427.

(207) Williams, D. E. G. *J. Chem. Phys.* 1987, 87, 4207-4210.

(208) Elser, V.; Haddon, R. C. *Nature (London)* 1987, 325, 792-794.

(209) Elser, V.; Haddon, R. C. *Phys. Rev. A* 1987, 36, 4579-4584.

(210) Fowler, P. W.; Lazeretti, P.; Zanasi, R. *Chem. Phys. Lett.* 1990, 165, 79-84.

(211) Pauling, L. Unpublished work.

(212) Haddon, R. C.; Elser, V. *Chem. Phys. Lett.* 1990, 169, 362-364.

(213) Schmalz, T. *G. Chem. Phys. Lett.* 1990, 175, 3-5.

(214) Fowler, P. W.; Lazeretti, P.; Malagoli, M.; Zanasi, R. *Chem. Phys. Lett.* 1991, 179, 174-180.

(215) Ajie, H.; Alvarez, M. M.; Anz, S. J.; Beck, R. D.; Diederich, F.; Fotiopoulos, K.; Huffman, D. R.; Krätschmer, W.; Rubin, Y.; Schriever, K. E.; Sensharma, K.; Whetten, R. L. *J. Phys. Chem.* 1990, 94, 8630-8633.

(216) Hare, J. P.; Krato, H. W.; Taylor, R. *Chem. Phys. Lett.* 1991, 177, 394-398.

(217) Reber, C.; Lee, L.; McKiernan, J. I.; Zink, J. I.; Williams, R. S.; Tong, N. W.; Ohlberg, D. A. A.; Whetten, R. L.; Diederich, F. N. *J. Phys. Chem.* 1991, 95, 2127-2129.

(218) Frum, C. I.; Engleman, R.; Hedderich, H. G.; Bernath, P. F.; Lamb, L. D.; Huffman, D. R. *Chem. Phys. Lett.* 1991, 176, 504-507.

(219) Haufner, R. E.; Conceicao, J.; Chibante, L. P. F.; Chai, Y.; Byrne, N. E.; Flanagan, S.; Healey, M. M.; O'Brien, S. C.; Pan, C.; Xiao, Z.; Billups, W. E.; Chiufolini, M. A.; Hauge, R. H.; Margrave, J. L.; Wilson, L. J.; Curle, R. F.; Smalley, R. E. *J. Phys. Chem.* 1990, 94, 8634-8636.

(220) Allemann, P.-M.; Koch, A.; Wudl, F.; Rubin, Y.; Diederich, F.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Am. Chem. Soc.* 1991, 113, 1050-1051.

(221) Hawkins, J. M.; Lewis, T. A.; Loren, S. D.; Meyer, A.; Heath, J. R.; Shabot, Y.; Saykally, R. J. *J. Org. Chem.* 1990, 55, 6250-6252.

(222) Hawkins, J. M.; Meyer, A.; Lewis, T. A.; Loren, S. D.; Hollander, F. J. *Science* 1991, 252, 312-313.

(223) Arbogast, J. W.; Darmayan, A. P.; Foote, C. S.; Rubin, Y.; Diederich, F. N.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Phys. Chem.* 1991, 95, 11-12.

(224) Hare, J. P.; Dennis, T. J.; Krato, H. W.; Taylor, R.; Alaf, A. W.; Bain, S. P.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* 1991, 412-413.

(225) Bethune, D. S.; Meijer, G.; Tang, W. C.; Rosen, H. J.; Golden, W. G.; Seki, H.; Brown, C. A.; de Vries, M. S. *Chem. Phys. Lett.* 1991, 179, 181-186.

(226) Bethune, D. S.; Meijer, G.; Tang, W. C.; Rosen, H. J. *Chem. Phys. Lett.* 1990, 174, 219-222.

(227) Dennis, T. J.; Hare, J. P.; Krato, H. W.; Taylor, R.; Walton, D. R. M.; Hendra, P. *Spectrochimica Acta*, in press.

(228) Johnson, R. D.; Meijer, G.; Bethune, D. S. *J. Am. Chem. Soc.* 1990, 112, 8983-8984.

(229) Johnson, R. D.; Meijer, G.; Salem, J. R.; Bethune, D. S. *J. Am. Chem. Soc.* 1991, 113, 3619-3621.

(230) Tycko, R.; Haddon, R. C.; Dabbagh, G.; Glarum, S. H.; Douglass, D. C.; Muijce, A. M. *J. Phys. Chem.* 1991, 95, 518-520.

(231) Yannoni, Y. C. S.; Johnson, R. D.; Meijer, G.; Bethune, D. S.; Salem, J. R. *J. Phys. Chem.* 1991, 95, 9-10.

(232) Haddon, R. C.; Schneemeyer, L. F.; Waszczak, J. V.; Glarum, S. H.; Tycko, R.; Dabbagh, G.; Kortan, A. R.; Muller, A. J.; Muijce, A. M.; Roseminkay, M. J.; Zahurak, S. M.; Makhija, A. V.; Thiel, F. A.; Raghavachari, K.; Cockayne, E.; Elser, V. *Nature (London)* 1991, 350, 46-47.

(233) Fowler, P. W. *Nature* 1991, 350, 20-21.

(234) Wilson, R. J.; Meijer, G.; Bethune, D. S.; Johnson, R. D.; Chambliss, D. D.; de Vries, M. S.; Hunziker, H. E.; Wendt, H. R. *Nature (London)* 1990, 348, 621-622.

(235) Wragg, J. L.; Chamberlain, J. E.; White, H. W.; Krätschmer, W.; Huffman, D. R. *Nature (London)* 1990, 348, 623-624.

(236) Chen, T.; Howells, S.; Gallagher, M.; Yi, L.; Sarid, D.; Lichtenberger, D. L.; Nebeany, K. W.; Ray, C. D. *Proceedings of Symposium G on Clusters and Cluster-Assembled Materials. Mater. Res. Soc. Proc.*; Averback, R. S.; Nelson, D. L.; Bernholc, J., Eds.; MRS Publications: New York, 1991.

(237) MacKay, A.; Vickery, M.; Klinowski, J.; Hare, J. P.; Dennis, T. J.; Krato, H. W.; Taylor, R.; Walton, D. R. M. Unpublished results.

(238) Fleming, R. M.; Sierrist, T.; Marsh, P. M.; Hensen, B.; Kortan, A. R.; Murphy, D. W.; Haddon, R. C.; Tycko, R.; Dabbagh,

(239) Soc., *Chem. Commun.* 1991, in press.

(240) Lichtenberger, D. L.; Nebenjy, K. W.; Ray, C. D.; Huffman, D. R.; Lamb, L. D. *Chem. Phys. Lett.* 1991, **176**, 203-208.

(241) Lichtenberger, D. L.; Jatiko, M. E.; Nebenjy, K. W.; Ray, C. D.; Huffman, D. R.; Lamb, L. D. *Proceedings of Symposium G on Clusters and Cluster-Assembled Materials, Mater. Res. Soc. Proc.*; Averback, R. S., Nelson, D. L., Bernholc, J., Eds.; MRS Publications: New York, 1991.

(242) *Proceedings of Symposium G on Clusters and Cluster-Assembled Materials, Mater. Res. Soc. Proc.*; Averback, R. S., Nelson, D. L., Bernholc, J., Eds.; MRS Publications: New York, 1991.

(243) Herbst, E.; Klemperer, W. *Astrophys. J.* 1973, **185**, 505-533.

(244) Dalgarno, A.; Black, J. H. *Rep. Prog. Phys.* 1976, **39**, 573-612.

(245) Herbig, G. H. *Astrophys. J.* 1975, **196**, 129-160.

(246) Herbig, G. H. *Astrophys. J.* 1988, **331**, 999-1003.

(247) Snow, T. P.; Seab, C. G. *Astron. Astrophys.* 1989, **213**, 291-294.

(248) Somerville, W. B.; Bellis, J. G. *Mon. Not. R. Astron. Soc.* 1989, **240**, 41P-46P.

(249) Léger, A.; d'Hendecourt, L.; Verstraete, L.; Schmidt, W. *Astron. Astrophys.* 1988, **203**, 145-148.

(250) Joblin, C.; Mailard, J. P.; d'Hendecourt, L.; Léger, A. *Nature* 1990, **346**, 729-731.

(251) Hoyle, F.; Wickramasinghe, N. C. *Astrophys. Space Sci.* 1986, **122**, 181-184.

(252) Rabilizirov, R. *Astrophys. Space Sci.* 1986, **125**, 331-339.

(253) Wright, E. L. *Nature (London)* 1988, **336**, 227-228.

(254) Duley, W. W.; Williams, D. A. *Mon. Not. R. Astron. Soc.* 1988, **231**, 969-975.

(255) Léger, A.; Puget, L. J. *Astron. Astrophys.* 1984, **137**, L5-L8.

(256) Allamandola, L. J.; Tielens, A. G. G. M.; Barker, J. R. *Astrophys. J.* 1985, **290**, L25-L28.

(257) Balm, S. P.; Kroto, H. W. *Mon. Not. R. Astron. Soc.* 1990, **245**, 193-197.

(258) McKay, K. G.; Dunne, L.; Kroto, H. W. Manuscript in preparation.

(259) Clayton, D. D. *Nature (London)* 1975, **257**, 36-37.

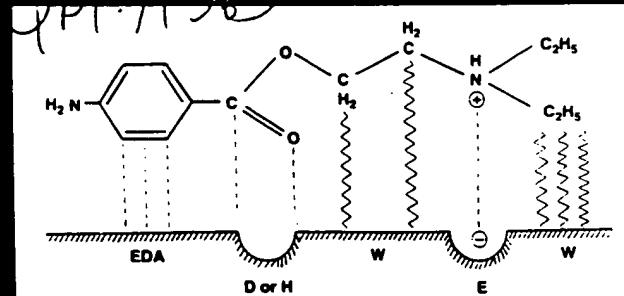
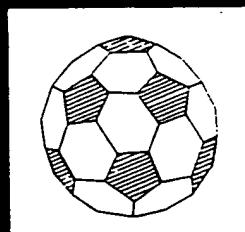
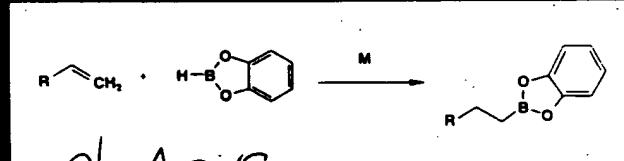
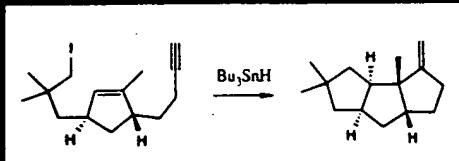
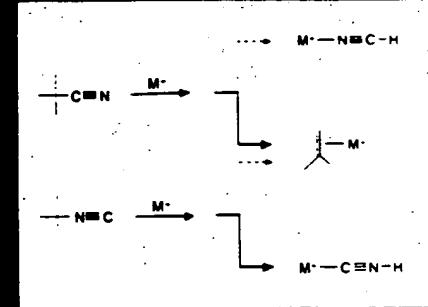
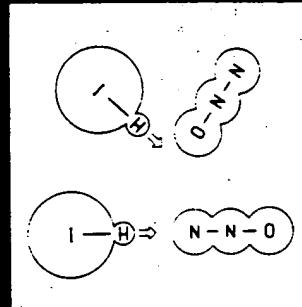
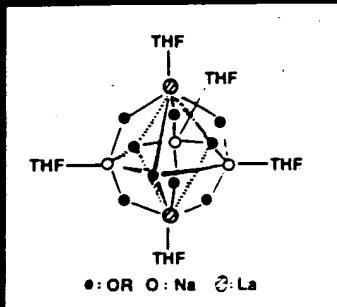
(260) Zinner, E.; Wopenka, B.; Amari, S.; Anders, E. *Lunar and Planetary Science XXI*, 1991, in press.

(261) Anderson, P. *The Man-Kzin Wars*; Niven, L., Eds.; Baen Publishing Enterprises, Simon and Schuster Distributors: New York, 1989; pp 168-169.

(262) Vittal, J. J. *J. Chem. Ed.* 1989, **66**, 282.

(263) Diederich, F. N.; Foote, C. S.; Whetten, R. L. *Chem. Eng. News* 1991, in press.

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